Universidade de Aveiro Departamento de Geociências
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Anabela Ferreira de Oliveira Cachada

Geoquímica e Qualidade Ambiental de Solos Urbanos
Geochemistry and Environmental Quality of Urban Soils

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Geochemistry and Environmental Quality of Urban Soils

Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Geoquímica, realizada sob a orientação científica do Doutor Armando da Costa Duarte, Professor Catedrático do Departamento de Química da Universidade de Aveiro e do Doutor Eduardo Anselmo Ferreira da Silva, Professor Catedrático do Departamento de Geociências da Universidade de Aveiro.

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palavras-chave

Solos urbanos; qualidade ambiental; contaminantes orgânicos; metais potencialmente toxicos; indústria química; Estarreja.

resumo

Os ecossistemas urbanos representam um elevado consumo de recursos, tendo um efeito insustentável no meio ambiente. Os solos urbanos são utilizados durante o desenvolvimento urbano e necessitam de ser geridos para serem preservados e deste modo manter o seu papel de suporte e aumentar a qualidade de vida. Sendo os solos considerados fontes e acumuladores de poluição é importante desenvolver metodologias para avaliação da qualidade ambiental de solos urbanos como ferramenta de gestão sustentável dos recursos.

As zonas urbanas são afectadas por uma enorme variedade de actividades antropogénicas, sendo as mais importantes o tráfego e a indústria. Estarreja é uma importante área industrial situada no noroeste de Portugal, estando o complexo químico localizado apenas aproximadamente a 1 km do centro urbano.

Assim, e de modo a obter uma caracterização geral da área de estudo, foram recolhidas informações acerca do clima, topografia, geologia, tipo de solo, dados ambientais (emissões para atmosfera, poluição da água, etc.), planeamento local, população, uso do solo e caracterização da indústria. Os pontos de amostragem foram depois seleccionados com base em fotografias aéreas, mapas de solo e observação no campo. De seguida foram seleccionados alguns indicadores da qualidade de solos urbanos, tendo em conta que um indicador útil para uma gestão sustentável dos solos deve ser sensível a mudanças na gestão. Finalmente, e com ajuda de instrumentos de SIG, foi possível obter uma visualização da variabilidade espacial dos parametros estudados. O estudo de indicadores de qualidade, aliado à informação recolhida inicialmente é essencial como apoio a processos de decisão, permitindo uma melhor sustentabilidade na gestão dos recursos urbanos. Permite ainda uma monitorização das mudanças na qualidade ambiental que ocorrem e definir quais as principais fontes de poluição que afectam os centros urbanos.

keywords

Urban soils; environmental quality; organic contaminants; potential toxic metals; chemical industry; Estarreja.

abstract

Urban systems represent high turnover of resources, having an effect on the environment in an unsustainable manner. Urban soils are used during urban development and needs to be managed if it is to be preserved and maintained its role in supporting and enhancing the quality of life. Since soil can be considered both as a source and as a sink of pollution, it is important to develop and validate a methodology for the assessment of environmental quality in urban soils, as a tool for sustainable resource management.
The urban areas are affected by a wide variety of anthropogenic activities, such as traffic and industry. Estarreja is a very important industrial area of Northwest Portugal, being the chemical complex located near (1 km away) the town centre of the urban area also called Estarreja.
Therefore, data about the climate, topography, geology, soil type, other environmental data (air emissions, water pollution, etc.), local planning, population (type and distribution), industry characterisation and distribution, land use, transports and energy inputs, were collected in order to have a general characterization of the study area. The sampling sites were chosen based on aerial photographs, soil maps and field observation.
Indicators of urban soil quality were then chosen taking into account that as a useful indicator of land management practices sustainability, a soil parameter must respond sensitively to changes in management. Finally GIS tool were used to show spatial variability of contaminant. The main usefulness of this study is the important information for decision-making, allowing a better sustainable resource management in very industrialized urban areas. These results of urban indicators, allied with data collected are essential for sustainable urban planning allowing a more efficient management of resources available as well as an effective control of state changes occurring in the environmental quality of urban ecosystems, particularly in what concerns urban soils. They also allow defining the main causes of pollution affecting urban areas.

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1. Introduction

Soils are part of the ecosystem, acting as an interface between the hydrosphere, atmosphere, biosphere and lithosphere. It provides functions as filtering, buffering, transformation and storage of contaminants and nutrients, decomposition of organic contaminants and groundwater recharge, protection and mineralization (Norra & Stüben, 2003). Nevertheless, these functions are limited and overuse can endanger the environment and the quality of life, therefore soils must be subject of sustainable urban planning development and legislation.

Human activities are damaging soils and leading to irreversible losses, for that reason, and as they are a limited resource, soils need to be conserved. Agricultural intensification, urbanization and industrialization are contributing to erosion, local and diffuse contamination and sealing of soil surfaces. Pressures on soils, associated to natural factors such as climate, have a significant impact on soil chemical, physical and biological characteristics. These changes in the environment may modify soil properties, such as pH, electrical conductivity (EC), organic matter content (OM) or cation exchange capacity (CEC) and therefore certain soil functions and the availability of contaminants may also be altered. As a consequence soil is degraded, being the main causes: erosion, compactation and crusting, acidification, salinization and sodification, accumulation of toxic elements and depletion of nutrients.

Soil protection is normally addressed indirectly through measures to protect water and air, or developed within a secondary protection. This is mainly due to soils great buffering capacities, slow reactions to contaminants and its natural spatial variability. The last one is a specific problem of the soil compartment that makes difficult the distinction between natural anomalies and those resulting from human activities (Mol *et al.*, 1998). In this context, it is very important the development of policies that take into account the role of soils, the problems arising from the competition among its multiple uses (ecological and socio-economical), and that aims towards the maintenance of its multiple functions. Therefore, a sustainable management of soil as a natural resource, together with air and water is a major environmental challenge.

Urban areas are the geographic focus of resource consumption and chemical emissions. As a consequence, urban soils receive a load of contaminants larger than those received in surrounding fields due to concentration of anthropogenic activities. Examples of contamination sources in urban environment include atmospheric deposition, industry, traffic and manipulation of pesticides and fertilizers. Contaminants can pass to the food chain by inhalation, ingestion and dermal contact of dust and particulate matter. Moreover, soil

contaminants may be recirculated by re-volatilization, in the water solution or uptaked by biota. Such processes contribute to reduce air and water quality and biomagnification of pollutants with consequent decrease in the standard of living, mainly in urban areas. Sealing and total erosion due to excavation are other factors that are consuming urban soils. These factors, allied with an increase in urban population (in European Union is increasing up to 80%) are acting as ecosystems factors leading to new soil properties. Urban systems represent, therefore, a high turnover of resources, having an effect on the environment in an unsustainable manner.

Since soil can be considered both as a source and as a sink of pollution, it is important to develop and validate a methodology for the assessment of environmental quality in urban soils, as a tool for sustainable resource management. An urban planning together with an efficient use of urban areas and re-utilization and recycling of abandoned areas can be important in sustainable development of cities. Therefore, and considering urban environment degradation, it is fundamental and urgent to develop comparable and reproducible methodologies of soil quality assessment in urban settings.

The purpose of this work is to study the geochemistry and environmental quality of urban soils. As a case study it was chosen Estarreja, a small city from northwest Portugal, notorious for its chemical industry. For the quality assessment of urban soils from Estarreja, data about the climate, topography, geology, soil type and other environmental data (atmospheric emissions, water pollution, etc.), were collected in order to have a general characterization of the study area. Socio-economic indicators were also collected, as these are driving forces for the formation of a city as environment. A general characterization of soils was first performed followed by the study of more specific indicators such as levels of potentially toxic metals and organic contaminants. Basic and multivariate statistical procedures and GIS tools were used to identify sources of pollution and discriminate natural and anthropogenic contributions as well as point sources of contamination. In conclusion, this study aims at identifying possible sources of contamination (industry, agriculture or the urban area), assessing the suitability of soil to its use and to contribute for land use planning in accordance to soil characteristics. To better understand the study a description of the adopted methodology was previously made.

2. Proposed methodology to evaluate soil quality: a tool for urban resource management

2.1. Urban soils issues

According to the European Community (EC, 2004) soils of urban areas have specific benefits and dis-benefits for quality of live spectra such as health, social, economical, technical and environmental qualities. These soils are defined as soils which occur within the boundary of an urban community and they include natural, man-modified and man-made soils. These last two types may occur outside the urban communities.

Urban soil is used during urban development and it needs to be managed in order to preserve and maintain its role of supporting and enhancing quality of life. The main functions of an urban soil are: the support of infra-structures, recreation/landscaping/leisure, preservation of air and water quality, life support (ecological), natural heritage, health cost reduction and heat balance. However, sealing soils, more than losing soils for agricultural and forestry, will limit ecological functions of soil, such as storage of carbon or habitat for unique biota. Indirect effects may be the fragmentation of habitats and disrupt of ecological corridors. Moreover, water runoff may increase, resulting in a higher risk of floods. Other problem is the accumulation of contaminants in urban soils that not only degrades soil quality but can also pose a health risk to humans and the ecosystem (Wong *et al.*, 2004). For example, in areas where public gardens and parks are exposed to significant pollution levels, dust from ground may have toxic effects as a consequence of inhalation or ingestion by humans, particularly children (Manta *et al.*, 2002).

The knowledge about processes of urban soil genesis and the role of soil in urban ecosystems is essential for environmental-impact assessments due to the fact that soil is an important source and sink of contaminants. Urban soils development does not only depend of natural factors as in natural areas, but also of the socio-economical processes, including planning that can become sometimes predominant factors. The genesis of urban soils is based on conditions that are not found in natural or agricultural systems. During urban development soils are damaged and modified especially by land use changes and engineering requirements and original soils are often buried, removed, compacted and contaminated. Sometimes local urban soil is replaced by foreign soil of inferior quality. In some cases these soils consist of slags, ashes, waste, building rubble, tar, sludge, etc, or mixed with natural substances. Other peculiar characteristics of urban soils are the unpredictable layering, poor structure and high concentrations of trace elements (Manta *et al.*, 2002). Therefore, hydrology, degree of sealing and compressing may differ from natural soils. An important issue related to urban areas is the diffuse pollution, being the main causes the combustion processes, the waste disposal from traffic, households and

industry, changes in land use type and intensity, the precipitation, the air temperature, humidity and soil parent material (Norra & Stüben 2003). As a consequence of all these specific characteristics, urban soils have specific soil chemistry, being the main factors responsible for the pattern: atmospheric deposition, waste disposal, construction activities, coal burning waste and sealing (Manta *et al.*, 2002; Norra & Stüben, 2003). Furthermore, in an urban environment it is possible to classify different land uses according to its influence such as traffic, industrial, commercial, disposal sites, cemeteries, housing and parks.

2.2. General characterization of urban ecosystems: data collection

A comprehensive preliminary characterization of the ecosystem is essential to define the set of soil properties to be assessed, in order to provide a suitable soil quality assessment of the urban area. It will also allow defining the criteria for selection of sampling sites and establish sampling and analytical procedures.

The main objective of data collection is to characterise the urban ecosystems by gathering all the available information about land use management. General data about climate, topography, geology, soil type and specific environmental data (such as atmospheric emissions and water pollution), are collected in order to have a general characterization of the study area. A socio-economic characterisation of the city is also important as some pressures on soil consumption may be socio-economic factors such as the high dependence of gross national income from land consumption (EC, 2004). Most of our modern social economic activities depend on the construction, maintenance and existence of sealed areas. Housing, mobility and communication, supply with goods and services, security, health, traditional construction and urban architecture demand sealing are also factors that will influence the soil use (EC, 2004). This way, it should be collected information about urban planning, population (type and distribution), industry typology and distribution, land use, transports and energy inputs. Therefore, and in order to perform a comprehensive assessment of the soil quality of an urban ecosystem, the following features should be considered:

- **History**: age of the city, traditional occupations, resources available through time, historical development, historical parks, historical buildings and infra-structures, archaeological sites, planning models used over time, historical industrial development;

- **Demography and socio-economic indicators**: size of the city, population density, evolution of resident population, employment and health statistics, education degree statistics, housing conditions, gross domestic product, degree of technological development, types of industry and commercial services;
- **Land use**: historic land use, present and planned land use, land use density, regulatory framework of territorial planning, percentage of sealed and urbanised land, percentage of forest, urban agricultural and green areas, percentage of derelict land, delimitation of the urban area, delimitation and area of the city centre, transport patterns and traffic intensity;
- **Natural conditions**: available natural resources, flood areas, topography and slope, ground stability, groundwater resources and hydrological features, geology (bedrock and soil types), biodiversity and protected habitats, species of special interest;
- **Climate**: temperature, precipitation, humidity, wind speed and direction, cloud cover, solar radiation;
- **Pollution sources**: characterisation of main driving forces for physical, chemical and microbiological pollution and their emissions – industrial, commercial, household, agricultural and gardening, waste management, traffic, construction, tourism and energy sectors; historical data on point and diffuse sources.

In conclusion, data collection in preliminary assessments of urban soil quality should allow: to define and characterise elements and components of the urban ecosystem under study; define patterns of soil uses; a preliminary evaluation of soil functions and of changes in natural features and their spatial distribution; identify natural habitats of special importance, potentially contaminated sites and potentially toxic elements and substances.

2.3. Sampling strategy and sample preparation of urban soils

Sampling and sample preparation procedures for the investigation of soils are regarded as the first and most important step towards a more comparable and reproducible analysis of soil (Wagner *et al.*, 2001), and must to be planned in accordance with the objectives of the study. In fact, when performing a sampling plan one has to keep in mind that the major objective of sampling is to be representative and that sampling and sample pre-treatment shall be “fit-for-purpose” (Barbizzi *et al.*, 2004; Kurfürst *et al.*, 2004).

Regarding urban soils, the level and spatial pattern of soil quality parameters need to be taken into account, and characterising this variability is an essential step, even though very complex, for an environmental survey. Therefore, the preparation of a sampling plan that include the sampling design for assessing soil quality/ contamination is a key step on the whole process as samples should be truly representative.

In what concerns to soil sampling there are some important issues that should be addressed: a) how methodologies might affect data quality; b) the sources of deviation or uncertainties; c) the comparability and representativeness of soil sampling or the sampling guidelines that are not harmonised (Theocharopoulos *et al.*, 2001). The usual geostatistical data treatment assumes a precise protocol for sampling as well as mapping of sampling sites. It requires also a minimum number of field measurements and analytical determinations to enable useful interpretation of the results. However, in the case of urban soils it is not always possible to collect a number of samples enough for the geostatistical analysis; besides, the choice of sampling sites is usually restricted to the available land (not sealed) and public areas.

A preliminary sampling strategy should be defined, by choosing potential sampling sites, based on interpretation of available documents such as maps, aerial photographs, satellite images and also on field observations. All information collected about the urban ecosystem should also be taken in consideration when defining the potential sites for sampling. An important question that should be answered before the sampling campaign starts is sampling density in urban area. It is important to have representative samples of different land uses, covering all the urban area. The land uses to be sampled should also be previously selected and they may include: ornamental gardens (OG), parks (PO), roadsides (RD), riverbanks (RB), kindergartens (KT), agricultural (AG) and railway sides (RL).

The sampling plan should also include a detailed scheme with instructions for sampling, pre-treatment and storage of samples. A sampling protocol should be established well in advance before the sampling starts and it should include the sampling equipment (corers, augers), quantity of sample to collect, cleaning of samplers and containers to hold the samples (depending on the parameter to analyse, e.g. inorganic vs. organic compounds). It should also include all the processing steps after sampling: when and how the samples will be transported to the lab; contamination controls procedures; samples pre-treatment and samples storage. It is also important to have a list of material needed for sampling and to define previously how each sample will be labelled, with a

unique sample code. A field data inventory should be also completed in the field, including information helpful when evaluating the results: a detailed description of the sampling area, including the site location/ age and land use considerations such as description of the surroundings, traffic intensity and possible contamination sources.

In conclusion, the main objectives when defining the sampling plan are the selection of sites to collect urban soil samples and how it will be performed the collection of samples. The first one includes the definition of sampling regimes (classes of urban soil to be considered) and the establishment of a sampling strategy (sampling sites/points carefully defined and the sampling design defined). Once again, the sampling plan will be dependent on the objectives of the study and materials and methods used for sampling, storage and analysis can not interfere with the analyte and/or matrix.

2.4. Definition and assessment of general indicators of urban soils quality

Defining soil quality in objective terms is very difficult as the concept is diffuse and it must reflect a range of social, cultural and economic factors as well as biophysical properties. Karlen *et al.* (1997), defined soil quality as '*the capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation*'.

However, many other definitions of soil quality can be found (Diack & Stott, 2001):

a) "Degree of suitability to the specific functions that soils perform in a given system".

b) "The capacity of the soil to promote the growth of plants; protect the watersheds by regulating infiltration and partitioning of precipitation; and prevent water and air pollution by buffering potential pollutants" (US National Research Council definition).

The difficulty in establishing only one definition comes from the variety of land uses, location, environments, types of soils and a general lack of understanding between the interactions of processes occurring within soil.

Soil quality requirements will be dependent of the application considered. For example, requirements for general purposes are basic requirements regarding plant nutrients, salt content, swell and shrink behaviour on wetting and drying, rewettability of the soil (hydrophobic behaviour), homogeneity of the soil material and soil pollution (Huinink, 1998). In urban soils the requirements may have to be adopted for applications such as ornamental planting, ornamental trees, herbaceous grass, road verges or construction. In

addition, although there are many indicators that reflect the current capacity of the soil to function, there are only a few that can predict the capacity of the soil to support a range of disturbance regimes. Moreover, soil quality cannot be measured directly from soil alone but inferred from soil characteristics and behaviour under specific conditions.

According to Diack & Stott (2001) there are two approaches to quantify soil quality: descriptive and indicative. The first one is concerned with the characterization of different attributes of quality and the second one with the identification of specific indicators or parameters that will assess the ability or capacity of an attribute to function in a desired manner. The objective is to identify and measure specific indicators to better define urban soil quality.

According to European Environmental Agency (EEA, 2005), an indicator is a measure, usually quantitative, that can be used to illustrate and communicate complex phenomena simply, including trends and progress over time. It provides a clue to a matter of larger significance or makes perceptible a trend or phenomenon that is not immediately detectable. Indicators should be chosen taking into account that as a useful indicator of the sustainability of land management practices, a soil parameter must respond sensitively to changes in management (Doran & Parkin, 1996). When characterizing soil quality over a short-time period, critical properties must also be sensitive to changes in soil disturbances and inputs into soil system (Diack & Stott, 2001). Moreover, methods to quantify soil quality must assess changes in selected soil attributes over time, but not changes influenced by short-term weather patterns. Soils and their indicator values vary because of differences in parent material, climatic conditions, topographic or landscape position, soil organisms, and type of vegetation. Interpreting indicator measurements to separate soil quality trends from periodic or random changes is a major challenge for researchers and soil managers.

Assessment of soil quality requires the definition of key indicators based on information collected in the initial assessment, according to city-specific situations, type of soil use and scope of the study. This choice should be made before preparing the sampling plan. In this study, a general characterization of soils has made, including pH, cation exchange capacity (CEC) and exchangeable bases, particle size distribution (clay, silt, sand), elemental analysis (CNHS) and organic matter. More specific analysis, to evaluate the extent and the main sources of pollution, include potentially toxic metals (Pb, Zn, Cd, Ni, Cu, Cr, Fe, Mn, and Hg) and organic compounds (PAHs, PCBs). Other parameters can be

measured, however this will depend on pollution sources known and available analytical capabilities.

After deciding which indicators will be analysed, analytical methods are chosen and QC/QA and assessment procedures for the analytical methods adopted and implemented. Analytical methods should be selected among those already available for soil quality, i.e. national and internationally accepted methods. Whenever possible standardized methods, e.g. ISO or EPA, should be chosen. Nevertheless, new or adapted methods may be devised to adequately meet the particular situation of the urban soils.

2.5. Data reporting using statistics and GIS tools

For data reporting purposes, statistics and GIS tools may be used. The use of descriptive statistics and bivariate analysis allow the structural description of the input data. The one-dimensional analysis can be considered as a useful tool for exploratory analysis of data and general characterisation of the studied variables. For the graphical representation of data histograms and box-plots may be used, as they are the easiest way of highlighting the type of distribution of frequencies and the existence of outliers. By using bivariated analysis (e.g. Pearson's correlation) it is possible to understand how the variables are related, by finding correlations between pairs of parameters and therefore assess the nature and strength of covariation between factors.

As in most of the environmental studies, each site is characterized by multivariate data sets and the application of multivariate statistics to quality assessment of urban soils is of great importance, since it is able to consider several variables simultaneously and therefore allows interpretations that are not possible with univariate statistics. Principal Component Analysis (PCA) is a method that depends on the mathematical extraction of eigenvectors and eigenvalues from a matrix of sample resemblance values (normally Person correlation values). Using matrix algebra, PCA extracts from the matrix of correlation coefficients a series of equations (components) which summarise the relationships between variables and account for the variation present in the matrix. These equations, or principal components, are used to calculate unique sample scores, which can be plotted to produce an ordination diagram (Waite, 2000). The aim is to reduce the dimension of spaces, or to represent the complexity of relationships between variables in the minimum number of dimensions, being the main advantage the identification of associations between variables.

Geographic Information System (GIS) is a collection of computer hardware, software, and geographic data for capturing, managing, analyzing, and displaying all forms of geographically referenced information (ESRI - [w_1]). The computer system allows managing spatial data that is organized to yield useful knowledge, often as coloured maps and images, but also as statistical graphics, tables, and various on-screen responses to interactive queries. It implies that location of the data items are known in terms of geographic coordinates (latitude, longitude). Thus, GIS have functional capabilities for data capture, input, manipulation, transformation, visualization, combination, query, analysis, modelling and output (AWI - [w_2]). GIS can integrate and relate any data with a spatial component, regardless of the source of the data (Figure 2.1).

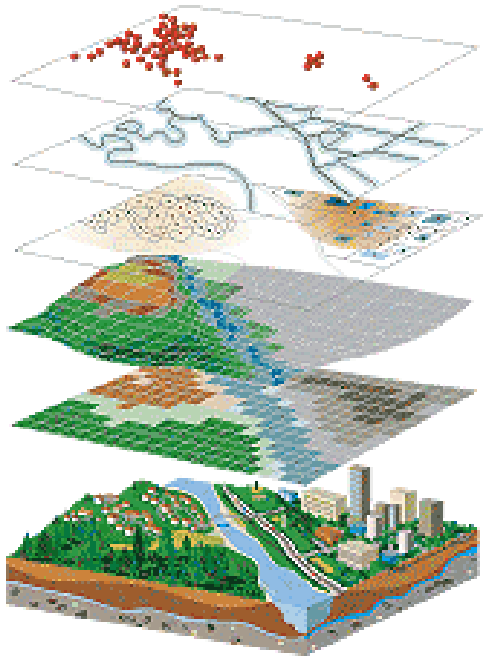


Figure 2.1 – Principles of GIS function, how it can integrate and relate data with a spatial component (ESRI- [w_1]).

The geographic information systems (GIS) are very useful in urban soils to show spatial variability of contaminants, being an easy way to identify, for e.g., sites exceeding the risk-based standards. With these tools, areas of potential or actual risk and areas were it is needed some kind of intervention can be identified. The analysis of the results obtained, compared with soil and land use (past and present) may lead to the identification of the main sources of pollution and degradation in the cities (former and present). Therefore, soil maps are important information for decision-making and can be

used for regulation purposes by Local Authorities since they show basic information for soil conservation and sustainable urban development (Norra & Stüben, 2003).

2.6. The importance of Quality Control/ Quality Assurance (QC/QA) in quality assessment of urban soils

"Quality control is the set of procedures used to measure and, when necessary, to correct data quality. Quality assurance is the set of procedures used to provide documentary assurance of the proper application of quality control and the resulting data quality" (Environment Canada, 2001). Quality assurance and quality control refer not only to the determination step but to all the steps of the analytical process, which in the case of soil quality studies can be considered as follows: definition of soil quality study, soil sampling, soil sample pre-treatment and storage, soil sample analysis, data reporting, conclusions and recommendations. Moreover, consistency in analysis can only be achieved if there is uniformity in procedures and nomenclature of all the steps mentioned (NEPC, 1999). The total uncertainty associated to the final results is, therefore, a sum of different contributions coming from the different steps of an analytical method: sampling, storage, treatment, analysis and data reporting.

The analysis itself can be nowadays considered under control or can be put under control following adequate precautions, due to the high performances of instrumental apparatus. Data treatment tends to be neglected as a QC/QA procedure, but it can also be a source of errors and therefore it should be under a strict control.

To control sample treatment QC/QA considerations should be integrated on the definition of the methodology, in order to assure representativeness and reliability of the results obtained. Standardized analytical methods (ISO methods) should be used whenever possible. Apart of this, the methods should be validated and quality of data assured by quality control measures. The QC/QA procedures includes the use of method blanks, that means processing the solvents and reagents in exactly the same way as samples giving the analytical signal that is not derived from the sample but from reagents, glassware, laboratory environment, etc. As a measure of accuracy, analysis of certified reference materials (CRM) should be implemented, especially of those provided by the Institute of Reference Materials and Measurements (IRMM, formerly BCR). They allow an evaluation of the performance of the overall analytical method (excluding sampling) rather than an evaluation of the extraction efficiency only. As CRM available are not always equal to the sample analysed (different matrix, different compounds and concentrations)

matrix fortified with analytes representative of the analyte class should also be used; however these spiking experiments can lead to an overestimation of the real extraction efficiency. Recoveries should be then checked and the results can be corrected or not for recovery. Quality control charts should be implemented as a tool for internal quality control. Variation between replicate analyses should be recorded for each process batch to provide an estimate of the precision of the method.

Sampling remains far from being under control, being this probably the single largest component affecting the value of any chemical measurement. Therefore a good analytical protocol must include sampling strategies free of contamination and loss and proper storage and stabilization of the samples, which is especially important when dealing with trace analysis. Other key issues regarding the QC/QA of results are, the representativeness of samples collected and the preparation of a precise sampling plan that is crucial to minimize the uncertainties associated to this step of the study.

3. Data collection and characterization of Estarreja urban ecosystem

3.1. Description of Estarreja urban area

The Municipality of Estarreja belongs to the district of Aveiro, and in terms of territorial divisions it is a part of the "Região Centro (NUT II)" and the "Unidade Territorial do Baixo Vouga (NUT III)". According to census of 2001 (INE, 2002) the Municipality of Estarreja, formed by Avanca, Pardilhó, Beduído, Veiros, Salreu, Canelas and Fermelã (Figure 3.1) has an area of 108.2 km^2, with a resident population of 28,182 individuals and a population density of 261 inhabitants/km^2 (INE, 2002). The urban perimeter of Estarreja has an area of 2.5 km^2 (Figure 3.2) and is a limited part of Beduído.

Estarreja Municipality has a close relation with the lagoon of Aveiro ("Ria de Aveiro") which supports a variety of biotopes (channels, islands with vegetation, mudflats, salt marshes and agricultural fields) with an important ecological value. Besides the natural conditions for harbour, navigation, fisheries (a very important activity for local inhabitants) and recreation, the coastal plain around the lagoon supports an intensive and diversified agriculture, a variety of heavy and light industries and a population of about half a million people are dependent on the environment surrounding Ria de Aveiro. This is, therefore, a very industrialized area, due to its five decades of chemical industry, with high demographic density and intensive agriculture.

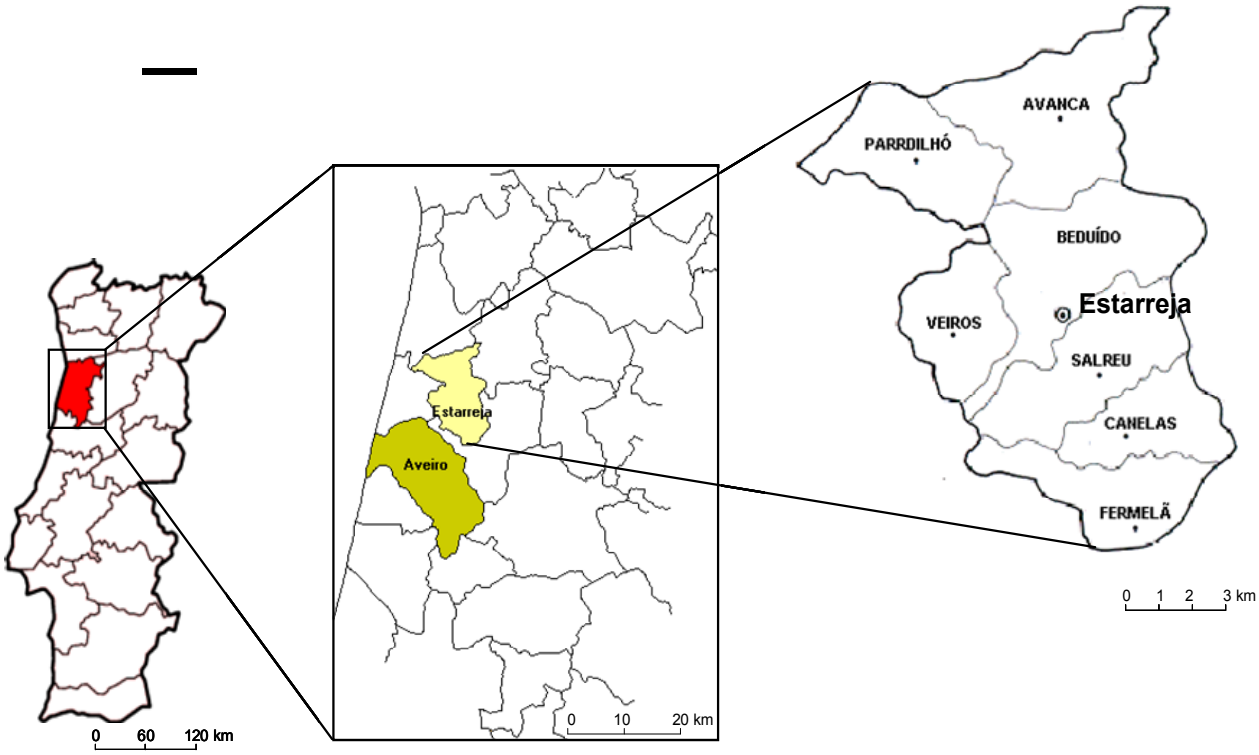


Figure 3.1 - The district of Aveiro and the Municipality of Estarreja.

The present and planned land use of Estarreja has been established by "Plano Director Municipal", a regulatory framework of territorial planning, where all information about location of green, urban, industrial and agricultural areas is available. This plan also establishes which are the areas of ecological relevance and delimitation of the urban area.

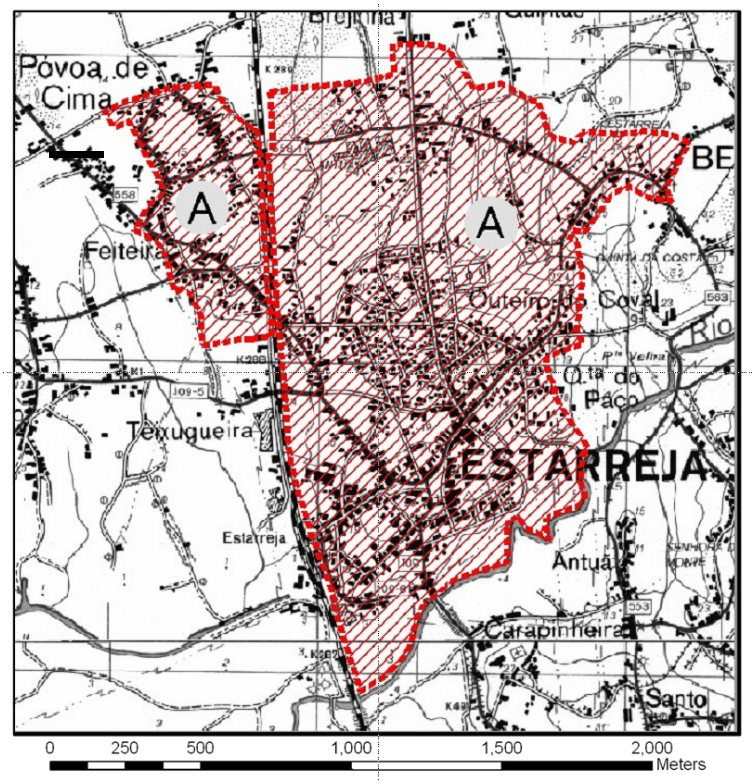


Figure 3.2 – Representation of the urban area of Estarreja (A) (CME, 2003).

3.2. Characterisation of the Estarreja urban ecosystem

3.2.1 Climate

Despite its relatively small extension, Portugal has a climate that varies significantly among regions and places. The main causes of this variation are the latitude, the distance to the sea and, for the regions of the coastal zone, the predominant orientation of the shoreline. Estarreja region is characterised by a warm climate with wet and dry seasons. A brief description is presented below (Instituto Meteorológico - [w_3]:

- **Average annual humidity**: values ranging from 79 to 88 %; the humidity results from the permanent evaporation verified in Ria and there is also a contribution of the humidity brought by summer breezes influenced by the Gulf Current.

- **Average annual temperature**: values ranging from 14.1 to 15.0 ºC; the lowest mean temperature range in winter is from 6.1 to 7.0 ºC and the range of the mean highest temperatures is from 22.1 to 23.0 ºC.
- **Average annual precipitation**: values ranging from 1201 to 1400 mm; the range of the mean values for winter is from 401 to 600 mm, while for summer is from 61 to 100 mm.
- **Predominance of winds:** from Northwest (NW) and North (N); in autumn, the predominance of NW diminishes, while increasing, gradually, the influence of the winds of SE and S.
- **Solar radiation/ hours of insolation**: from 110 hours in December to 320 hours in July; the total annual is from 2601 to 2700 hours.

3.2.2 Geology and soil type

Regarding geology, Estarreja is located in the Aveiro´s sedimentary basin. This basin is constituted by Quaternary units consisting of alluvium, sand dunes, old beach and terrace deposits that occur regionally as a superficial layer or as layers of variable thickness (maximum thickness is 25 to 30 m). The Modern Deposits are a system of beaches and fluvial terraces in steps, of detritic nature and granolumetries from fine to coarse (Barradas, 1992; Azevedo, 1999). They are represented by modern alluvions that form the littoral regions and sand dunes, being the last ones very significant all over the littoral extending to interior. This sedimentary basin is, in the north-eastern edge of the basin where Estarreja is located, only a dozen meters thick but as the structure plunges to the west, it may attain several tenths of meters (Costa & Jesus-Rydin, 2001). Concluding, three lithological units may be individualised in this Quaternary formation:

- the upper unit, composed of dune sands and alluvium silt-clayey sands, covered by organic topsoil;
- the intermediate unit, very heterogeneous, with irregular geometry, due to sudden vertical and horizontal geologic variations;
- the lower unit formed by loose conglomerates.

The Quaternary deposits overlay the bedrock, constituted by Paleozoic and Precambrian rocks in the north, or the Cretaceous formations in the rest of the region as shown in Figure 3.3. Figure 3.4 shows the detailed geology of Estarreja region in a scale of 1:50.000.

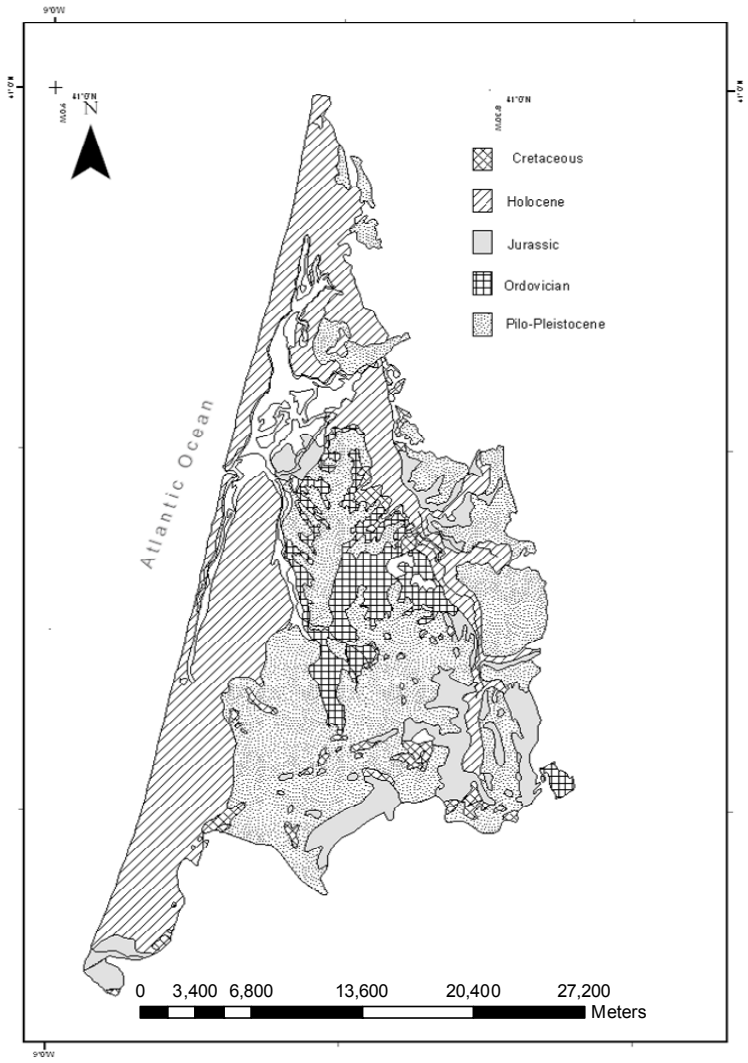


Figure 3.3 - Geology of the lower Vouga sedimentary basin, 1:25000 (from Carta Geológica de Portugal, 1972).

Soils in the area under study are mainly podzols, mainly found in sand dunes and low terraces (5-8 m), yet Cambisols can also be found (Ferreira, 1993; Azevedo, 1999). The horizons of these soils are well defined and it's important to note the existence of the B illuvial horizon (darker than adjacent ones due to accumulation of organic matter and sesquioxides) and the E elluvial (strongly lixiviated). The normal profile of a podzol has the horizons O-A-E-BHs-Bs-C.

Podzols, according to the Portuguese classification, are divided in two sub-orders: hydromorphic (Haplic) and not hydromorphic (Gleyic). The families more represented in the study area, are differentiated by the original material and by the cementation grade of Horizon B as follows (Azevedo, 1999):

- Pz – Podzols not hydromorphic without “Fe/Al pan”, of sands (Gleyic podzols)
- Ap – Podzols not hydromorphic without “Fe/Al pan”, of sands (Gleyic podzols)
- Pzh – Podzols hydromorphic with “Fe/Al pan”, of sands (Haplic podzols)
- Aph – Podzols hydromorphic without “Fe/Al pan”, of sands (Haplic podzols)

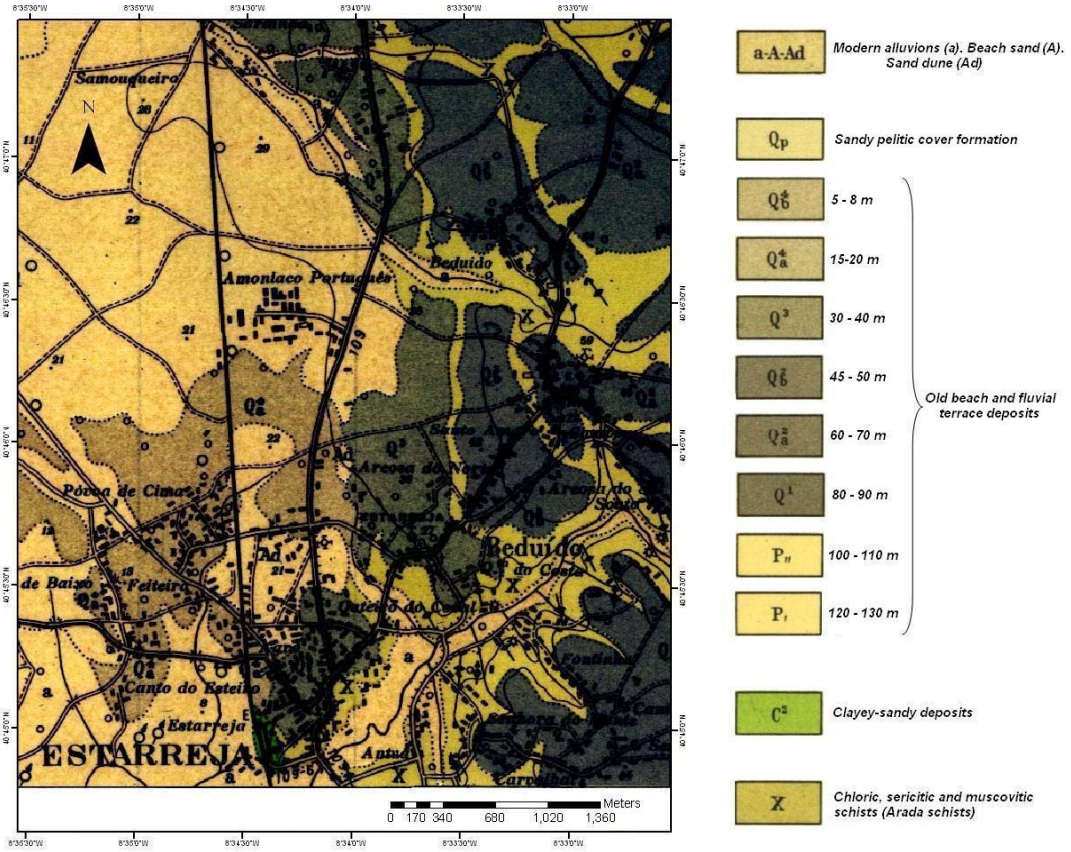


Figure 3.4 – Detailed Geology of Estarreja, 1:50000. Extracted from Carta Geológica de Portugal, 13C. (Teixeira & Zbyszewski, 1976).

Podzols are characterized by having low nutrient status, sandy texture, high C/N ratio, low CEC, fast permeability and low pH value and therefore they are infertile soils, being their agricultural use limited. Inácio *et al.* (1998) described the soils of Estarreja as permeable acidic sandy soils with low humus content. These soils have normally low retention capacity and they represent a potential risk of contaminants transfer in the soil–water–plant system. They are normally reserved for coniferous forestry, low intensity grazing or are left fallow. However, if fertilizers, liming and irrigation are practised reasonable yields of arable crops may be achieved. The main problems found when growing crops regards to aluminium toxicity, restriction of nitrification and phosphorus deficiency. Furthermore, podzolization results from the acidification of humus with the

formation of high quantities of organic compounds that migrate to the lower horizons, leading to the leaching out of iron and subsequent accumulation in lower horizons. As a result, a thin iron pan which is impervious is formed and they may then have hydromorphic properties.

3.2.3 Hydrogeology

One of the most important local resources is the Aveiro multilayer quaternary aquifer that covers an area of 650 km^2 in the occidental meso-cenozoic sedimentary basin (Condesso de Melo, 2002) and can be divided in 3 units, installed in sandy loose formations: the upper, the middle and the lower aquifers. Figure 3.5 shows the upper and the lower aquifers.

The superficial (upper) aquifer is constituted by recent deposits of alluviums and sand dunes from Holocene age. These deposits are abundant in the western part along the coast and inland along most of the riverbeds. The average thickness ranges between 8 to 10 m, rarely exceeding 20 m of total thickness. They form a highly permeable (20 to 30 md^{-1}) shallow aquifer with an area of 500 Km^2 (Condesso de Melo *et al.*, 2002). The aquifer receives direct or indirect recharge by infiltration of rainwater and irrigation, and the discharge occurs in sea, in the lagoon, in the hydrographical network or in other adjacent aquifer levels, since induced by positive hydraulic gradients (Condesso de Melo *et al.*, 2002). It should be highlighted that there is a piezometric depression in the Estarreja area that can be due to its intensive exploration (Condesso de Melo, 2002; INAG - [w_4]).

The lower aquifer, hydraulic free, is formed by old beach deposits and fluvial terraces from the Pilo-Pleistocene. These deposits are predominantly coarse sands, gravel pebbles, which mainly occur along the eastern part of the region, where they overlay either Cretaceous or Triassic formations. The thickness area ranges between 10 to 20 m and the average permeability range from 5 to 10 md^{-1}. The natural gradient in the terrace deposits is from west to the east (0.004) where they discharge to the principal rivers that flow in the area (Condesso de Melo, 2002), being the principal hydrographic basins: Vouga, Mondego, Ribeiras da Costa and Mangas das Ribeiras da Costa (in a total of 924.9 km^2). Another important characteristic of this region is the complex network of channels from the lagoon (Ria de Aveiro) and the delta of River Vouga.

This coastal aquifer is particularly vulnerable to saline intrusion but also, due to the high permeability of the sandy deposits and shallowness ground water table, it is extremely vulnerable to agricultural, urban and industrial contamination. It is known that in

the Estarreja municipality 79 % of the water from wells is unsuitable for consumption due to chemical contamination and 73 % due to bacteriological contamination (CME - [w_5]). Furthermore, in this region there has been common practice to abstract water from the superficial aquifer for drinking, industrial and agricultural purposes. Therefore, appropriate management and conservation policies should have been implemented in the region a long time ago.

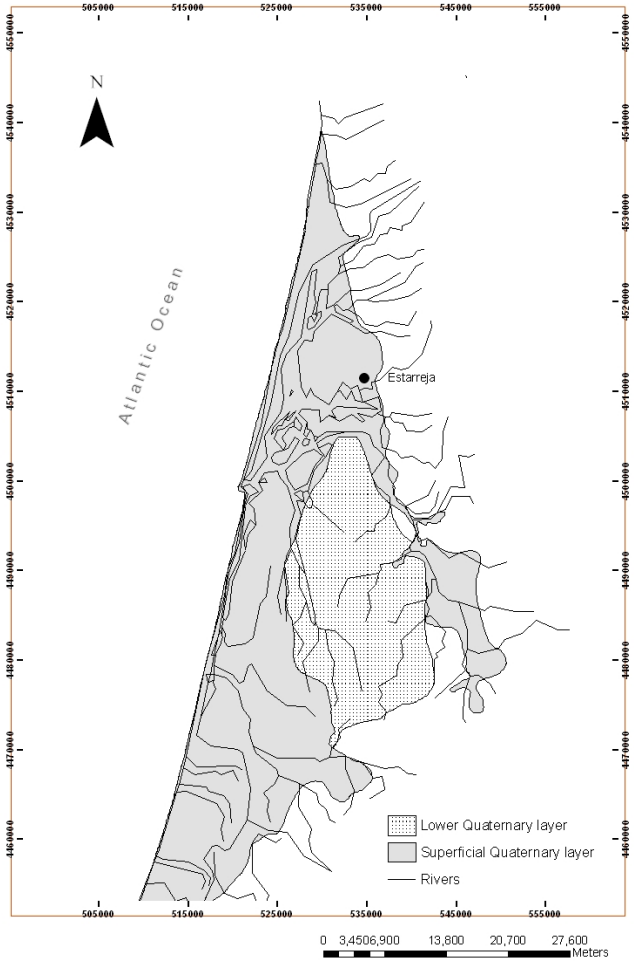


Figure 3.5 – The superficial and lower layers of the Aveiro multilayer quaternary aquifer and the region river basins (INAG - [w_4]).

3.3. Population and socio-economic indicators

Table 3.1 contains some indicators for Estarreja municipality, including general indicators, demographic indicators, economic activity and social indicators.

Table 3.1 - Summary of some indicators for Estarreja municipality (INE, 2002).

General Indicators		Unit	Year
Total surface	108.4	km^2	2004
Population density	261.0	hab/km^2	2004
Resident population	28,182	people	2001
	26,742	people	1991
Private household	9,196	-	2001
Institutional household	9	-	2001
Private dwellings (permanent)	11,661	-	2001
Private dwellings (temporary or mobile)	64	-	2001
Collective dwellings	17	-	2001
Buildings	10,424	-	2001
Demographic Indicators			
Live births	252	-	2004
Deaths (total)	317	-	2004
Birth rate	8.9	‰	2004
Mortality rate	11.2	‰	2004
Ageing index	109.1	%	2004
Resident household units	8,360	-	2001
Resident population changes	5.4	%	1991 to 2001
Economic Activity			
Accommodation (capacity of hotels)	18	places	2004
Companies' headquarters	674	-	2004
Companies of the primary sector	1.9	%	2004
Companies of the secondary sector	28.0	%	2004
Companies of the tertiary sector	70.0	%	2004
Sales on Companies Headquarters	600,423	thousands €	2004
Banks	12	-	2003
Buildings (total)	130	-	2004
Residential buildings	99	-	2004
Building Permits	128	-	2004
Building Permits for Residential Buildings	102	-	2004
Households	2.5	MWh/consumer	2003
Industrial power consumption	1,083.2	MWh	2003
Unemployment rate	5.7	%	1991
	6.7	%	2001
Social Indicators			
Physicians	1.1	per 1000 Inhabitants	2003
Pharmacies	0.2	per 1000 Inhabitants	2003
Hospitals	1	-	2003
Infant mortality (average)	2.1	‰	1999 to 2003
Illiteracy rate	8.7	%	1991
	7.2	%	2001

The basis of the economy in Estarreja is the secondary sector with a total of 6011 persons employed in 2003. From 1991 to 2001 the primary sector has experimented a significant decrease (-56.7%) while the tertiary sector has been more important for the

economy of the municipality (INE, 2002). These changes don't seem to have any significant effect in the resident population from the municipality, being the variation between 1991 and 2001 of 5.4% (Table 3.2). There was an increase in the resident population from Beduído, where Estarreja is located, meaning that population can be increasing in the urban area. When looking to the population distribution it's possible to say that this municipality is characterized by a having a high percentage of young people (Figure 3.6).

Table 3.2 – Variation and population density of Estarreja Municipality between 1991 and 2001 (INE, 2002).

	Area (km^2)	Resident Population		Variation (%)	Population Density 2001 (hab/km^2)
		1991	2001	1991/2001	
Avanca	21.5	6426	6474	0.7	301.1
Beduído	20.2	6731	7794	15.8	385.8
Canelas	10.2	1498	1486	-0.8	145.7
Fermelã	13.0	1580	1482	-6.2	114.0
Pardilhó	15.9	4234	4175	-1.4	262.6
Salreu	16.2	4157	4153	-0.09	256.3
Veiros	11.2	2116	2618	23.7	233.7
Municipality	108.2	26742	28182	5.4	260.4

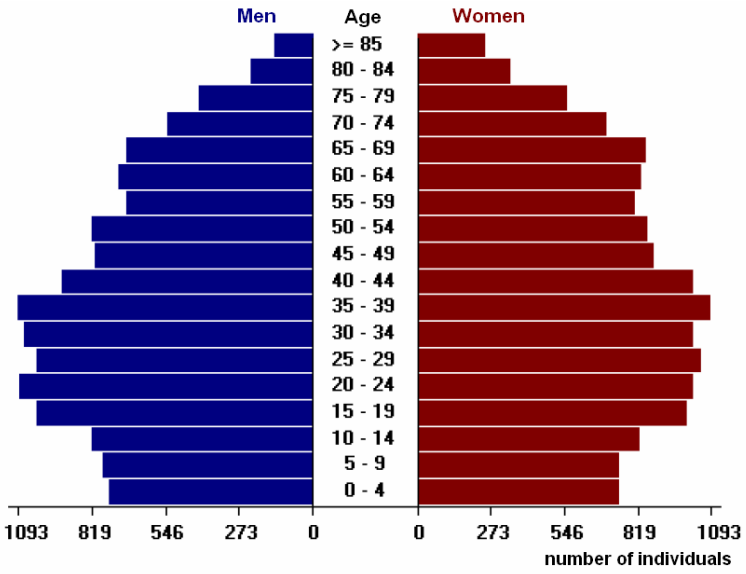


Figure 3.6 - Distribution of population in Estarreja municipality by age and by sex in 2001 (INE, 2002).

The socio-economic factors have an important influence in land consumption. Housing, mobility and communication, supply with goods and services, security, health, traditional

construction and urban architecture are the main factors responsible for pressures in the urban environment. Estarreja is a small city, with a small urban area that includes some agricultural areas. The main pressures are the industry near the centre and the moving of population to town centre.

3.3.1 The industry in Estarreja region

Table 3.3 shows the distribution of labourers in the industrial activities for Estarreja Municipality and for the Aveiro´s District in 2003 (AIDA - [w_6]). Besides the utmost importance of chemical industry (for which Estarreja is mostly known), other industrial activities can also be found in the municipality, such as food and drink, wood, cork, textiles and leather. However, agriculture is the most important economic sector (the main productive source are animal sector and corn farming).

Table 3.3 - Distribution of labourers in industries of the District of Aveiro and of Estarreja in 2003 (data from AIDA - [w_6]).

Industrial activity	Estarreja	Aveiro´s District
Food and beverages	1108	12499
Fabric	53	9697
Clothing and dyeing	87	4392
Leather and leather product	2	29744
Lumber processing	121	8189
Cork	2	13429
Pulp, paper and sub products	24	3370
Edition, impression and reproduction of recorded information	51	2317
Chemicals	731	2389
Production of rubber articles and plastic	35	6955
Production of other non-metallic mineral products	104	17373
Metallurgies	2	4360
Factories of metallic products (except machines and equipments)	704	24415
Machines and equipment	58	12137
Production of electrical devices	24	6914
Electronics	85	378
Production of vehicles, trailers and semi-trailers	3	7338
Production of other transportation materials	3	2967
Furniture factories and other non-specified industries	291	9875

Processing industries play a major role on local economy (33.4% employment), being the sector of metallurgies and metallic products the one that generates more employment (4.9%) (INE, 2002). In the second most important sector arise the food, beverages and tobacco industries, with 4.5%. In the 50's and 60's the production of chemicals and fibbers (synthetic or artificial) played the principal role as source of jobs in the municipality of Estarreja. Corroborating the observed gradual decrease in the importance of this sector, it should be noted that in 1991 this was the most important sector in a matter of employment offer and it turned, after ten years, into the fourth activity creator of jobs, highlighting once more the deep restructure of the local industry. In spite of the crisis in the chemical industry is often related with the increase in the cost of energy (Reis *et al.*, 1996), the modernization of the facilities is also responsible for the decrease in the need of labour. However, it is remarkable that almost 30% of the labourers in the chemical industry of the district are working in Estarreja.

The major part of chemical industry is located inside the chemical complex called "Complexo Químico de Estarreja (CQE)", an industrial area of 1 km^2, located at 1 km from the Estarreja town centre (which has an area of about 2.5 km^2). The most significant industrial units in CQE are:

- **Quimigal** [w_7]: installed in 1952, produced ammonium sulphate, from sulphuric acid and ammonia, since the beginning, and nitric acid and ammonium nitrate since 1974. These productions stopped in the early 1990s and a new unit (aniline de Portugal) started in 1978 for the production of nitric acid, aniline and nitrobenzene, which is still running. Other products are chlorine, sodium hydroxide and hydrogen. Since 1990, electrolytic cells with mercury cathodes have been substituted by membrane technology.
- **Uniteca** [w_8]**:** working since 1956 to produce chlorine, sodium hydroxide, hydrogen and derivate compounds as sodium hypochlorite and hydrochloric acid from rock salt, using until 1992 electrolytic cells with mercury cathodes.
- **Cires** [w_9]**:** the plant started up in 1963 producing only suspension PVC (S-PVC), being pioneer in the manufacture of thermoplastics materials. In 1982, emulsion PVC started to be manufactured for paste grade resins, the VICIR-E.
- **Dow Portugal** [w_{10}]**:** producing since 1978 isocyanide polymers of aromatic base and polystyrene polymers for thermal isolation.

3.3.2 Transport facilities

The resident population is mostly settled along the major road that crosses the municipality in the North-South direction (EN 109), which was during decades one of the main connections between the north and centre of coastal Portugal. Other transportation facilities are listed below:

- Roads – IP1, IP5
- Railroad – "Linha do Norte"
- Lagoon: Esteiro de Estarreja

3.4. Environmental Quality of Estarreja

3.4.1 Emissions from nearby industry

In a context of a lack of information about environmental issues, together with intensive industrial activity, during decades, direct discharge of effluents into natural water streams and uncontrolled waste disposal on ground were practiced (Hall, 1982; Pereira *et al.*, 1997; Costa & Jesus-Rydin, 2001). Since 1950s until 1975, the liquid effluents were discharged directly into manmade water streams (Vala de S. Filipe, Vale de Breja and Vala do Canedo), being transported for several kilometres through the agricultural fields, mainly to the river branch named Esteiro de Estarreja that ends in a lagoon basin called "Laranjo" (Barradas *et al.*, 1992; Inácio *et al.*, 1998, Costa & Jesus-Rydin, 2001). The liquid effluents from these industrial units contain mainly aniline, benzene, monochlorobenzene, mononitrobenzene, arsenic, mercury, zinc and lead (Batista *et al.*, 2002). Until 1990 Quimigal and Uniteca used electrolytic cells with mercury cathodes, but they have been substituted by a cleaner technology, membrane cells, being this conversion finished in 1998. Therefore Hg is one of the most concerns of this area. Several studies where conducted in Estarreja in order to assess the local contamination, but most of them where mostly focused in the contamination near the industrial complex (Inácio *et al.*, 1998; Costa & Jesus-Rydin, 2001; Batista *et al.*, 2002) and with the contamination through river streams leading to the Ria de Aveiro Lagoon (Abreu *et al.*, 1998; Pereira *et al.*, 1998; Monterroso *et al.*, 2003; Coelho *et al.*, 2005). Other studies conducted in this area include the study of Hg in plants, biota and in the water column from the lagoon (Ramalhosa *et al.*, 2001; Pereira *et al.*, 2005; Coelho *et al.*, 2006). It has been reported high concentrations of toxic pollutants, mainly potentially toxic metals and metalloids (namely As, Hg, Pb and Zn), in the soil of the industrial area, however much higher concentrations were found in the sediments of the water streams, several

kilometres away from the industrial complex (Costa & Jesus-Rydin, 2001; Batista *et al.*, 2002). Moreover, it is estimated that, in spite of the strong reduction on the input since 1994, it will be needed many decades until the Lagoon recovery (Pereira *et al.*, 1997; Abreu *et al.*, 1998).

Inácio *et al.* (1998) concluded that air contamination was higher next to the emission point inside the industrial perimeter decreasing with distance. In terms of air emissions of pollutants monitored in a station located inside the urban perimeter, the medium daily emission of SO_2 was 1.9 μg/m^3 in 2006 (Instituto do Ambiente - [w_{11}]), for particulate matter less than 10 μm (PM10) in the same year the medium value was 35 μg/m^3/day, and in what concerns NO_2 the value is 19.6 μg/m^3/day. These emissions are mainly from industrial activities.

The Air Quality Index (Instituto do Ambiente - [w_{11}]) for Estarreja area is shown in Figure 3.7. This index is a result of an arithmetic average of each pollutant concentration in all stations of the area. The values are compared with ranges of concentrations associated with a colour scale, with major importance given to the most toxic pollutants.

Emission data can also be found in the European Pollutant Emission Register (EPER - [w_{12}]). EPER was established by a Commission Decision of 17 July 2000. The EPER Decision is based on Article 15(3) of Council Directive 96/61/EC concerning integrated pollution prevention and control. EPER contains data on pollutant emissions to air and water reported by around 10,000 large and medium-sized industrial facilities in the former 15 EU Member States, Hungary and Norway. Fifty pollutants are covered and all reported emissions data are publicly accessible through the EPER website.

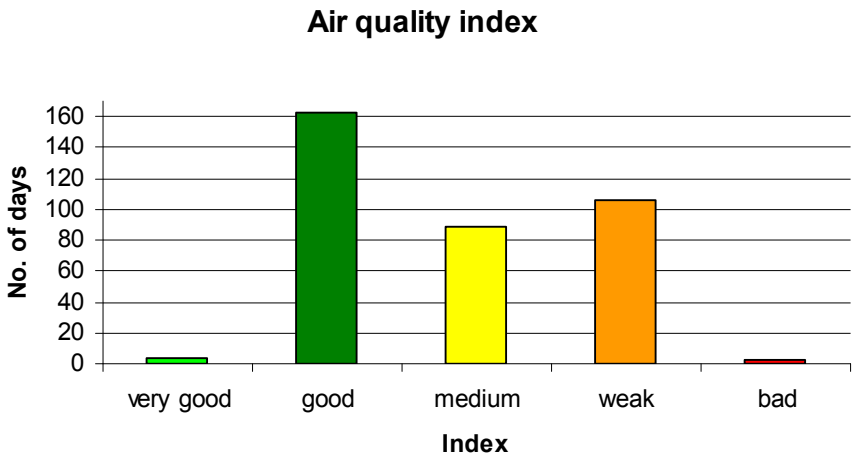


Figure 3.7 - Air Quality Indexes for Estarreja during 2005.

Figure 3.8 shows the activities in the region of Aveiro. In yellow are the industries settled in the Municipality of Estarreja, while in pink refer to two pulp and paper industries located in the Municipality of Aveiro. Table 3.4 shows emissions from the main industries of Estarreja reported to the EPER, including emissions to water and air, measured or calculated. Other industries in a 15 km perimeter from Estarreja and included in EPER inventory, reported emissions of hazardous pollutants, some of them important to the present study: cadmium, chromium, cooper, nickel, lead, zinc, halogenated organic compounds, carbon monoxide, volatile organic compounds, nitrogen oxides, sulphur oxides, phenols, cyanides, nitrogen, phosphorus.

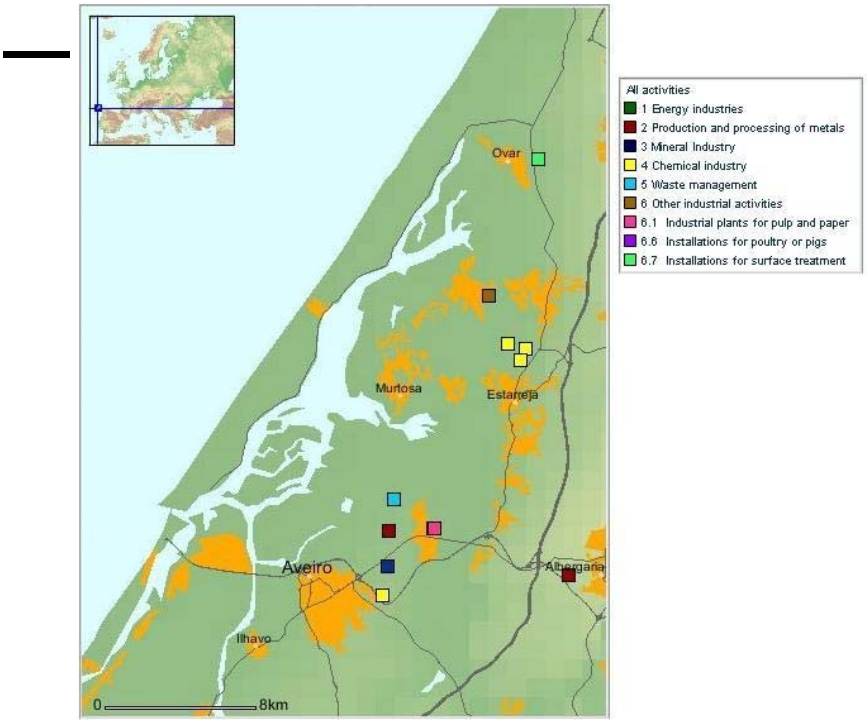


Figure 3.8 – Localization of the activities reported in EPER [w_{12}] for the region of Aveiro.

Table 3.4 - The emissions reported to the EPER [w_{12}] in the studied region for the year 2004.

Industry	Compounds	Emissions to air (tons)	Emission to water (tons)	Type of data[3]
Quimigal	Nitrogen oxides, NOx	251	-	M
	Nitrous oxide (N_2O)	902	-	E
	Benzene	1.80	-	M
Uniteca	Mercury and its compounds	-	0.00714[1]	M
	Chlorides	-	3,780[1]	M
Dow Portugal	Chlorides	-	25,500[1] 5400[2]	M
Companhia Industrial de Resinas Sintéticas, CIRES, S.A."	Hydrofluorocarbons (HFCs)	0.6	-	C
	Nitrogen oxides, NOx	598	-	M
	Sulphur oxides (SOx)	176*	-	M
	Cadmium and its compounds	0.123*	-	M
	Total Organic Carbon (TOC)	-	148[2]	
	Nickel and its compounds	0.096	-	M

[1]Direct release; [2]Indirect discharges (transfer to an off-site waste water treatment); [3]M = Measured; C = Calculated; * Data from 2001 report.

4. Sampling plan and strategy adopted for Estarreja

The definition of a written sampling plan (sampling protocol) with a detailed description of procedures to be followed is one of the first steps of the Quality Control/Quality Assurance (QC/QA) strategy. The sampling plan for Estarreja took into account the considerations mentioned in the previous chapter. The sites were previously selected, the sample strategy established and samples collected. The sites selected were not always feasible for sampling, and the network had to be kept open and adopted to verification of the field conditions. The procedures adopted for sampling and sample pre-treatment were based on ISO (ISO, 1994a) or USEPA (1996a) methods.

4.1. Sampling design of Estarreja urban soils

Sites were selected in order to cover the urban area and to have enough number of samples for each land use selected. The land uses selected were: ornamental gardens (OG), roadsides (RD), parks (PO) and agricultural (AG). Some samples were collected outside the urban area in order to compare results with the city centre and to assess what are the major influences in the quality of the soils, i.e. the urban area itself or the chemical industries near the town centre. It was decided to collect in agricultural sites because there are many agricultural areas within the city area, being an important use of the soil in Estarreja. Two sampling depths were considered (0-10 cm and 10-20 cm) in order to assess differences between layers. For each sampling site one of the following sampling regimes was adopted (Davidson & Urquhart, 2002):

a) Sampling Regime 1

Applicable to larger, visually homogenous, areas of soil where the entire area can be defined as a single "site" and where it is desirable to obtain an indication of the average soil quality. This could include, for example, areas within parks, gardens, cemeteries, forested or agricultural areas (typically > 1 ha). First the area of interest is defined and then divided into a regular grid. The sampling points may be randomly select i.e. a number of cells from the grid (typically sampling density ~ 20 per hectare) or collect a composite sample every 1-3 ha (Figure 4.1). A single sample from each sampling point is collected and then combined to form the bulk sample for the site.

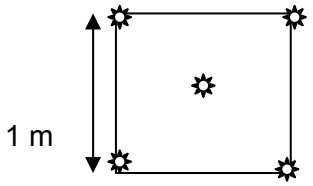


Figure 4.1 – Scheme for composite samples.

b) Sampling Regime 2

Applicable to smaller, visually homogeneous, areas of soil. This could include, for example, a flowerbed in a small ornamental garden, or a single allotment. An area of ~ 1 m^2 is defined and a sample close to each of the corners of the square and one from the centre is collected and then combined to form the composite sample for the site. The area should, as far as possible, be typical of the site and removed from point sources of contaminants such as metal fence posts etc.

c) Sampling Regime 3

Applicable to areas such as roadsides and riverbanks, where it may be important to determine average soil quality along a length of the roadside or bank. A transect along a roadside or riverbank (e.g. ~ 50 m in length) is defined and a sample is taken from one or more sampling points (e.g. every ~ 10 m along the transect). Samples are then combined to form the bulk sample for the site.

4.2. Sampling scheme and instructions

After defining each one of the sampling points on the field, surface vegetation is removed. For each sample, a "site Sampling Record" (Annex I) is completed at the sampling site. This record has details on: sample identification, sample log record (sampling site name, date and time of collection, GPS coordinates, sampling conditions, relevant sample site observations, signature of the sample collector(s)) and chain of custody record (record of personnel handling samples on the field). Care should be taken to ensure that the proximity of road (distance from the road and traffic intensity) or another potential pollution source is indicated and described. A chain of custody record (record of personnel handling samples on the field) was also kept. Table 4.1 shows a resume of sampling procedures for different purposes.

4.2.1 Procedure to collect urban soil samples

- Use a stainless steel spade to dig the hole and plastics spades for sampling collection;
- Take samples at two depths (0-10 cm and 10-20 cm);
- Collect samples according to procedures described for inorganics (4.2.2) and organics (4.2.3);
- Use GPS to register location of sampling sites;
- Follow QC/QA directions for soil sampling: use of "Site Sampling Record" for each sample.

Sample labelling and transport:

Each site and each sampling depth has a unique code. A standard sampling code should be used, where the number is the number of the site. As an example, the first soil sample, for the 0-10 cm depth is labelled as "EST.OG.01.SF", which stands for "Estarreja" (EST), "Ornamental Garden" (OG), site number 1 (01) and surface sample (SF). At the same site the subsurface sample (10-20 cm) is labelled as "EST.OG.01.SB".

Cleaning of tools:

All sampling equipment was cleaned with distilled water and paper towels, between usages. Soil samples were handled using plastic gloves (except for organics).

4.2.2 Sampling procedure for inorganics

Around 2 kg of soil was taken from the 10 cm top layer with a plastic spade, and kept in a labelled plastic bag (Table 4.1). The same is done for the 10-20 cm layer. Samples were stored in plastic bags, labelled, placed in boxes and transported to the laboratory.

4.2.3 Sampling procedure for organic compounds

Plastics were avoided because phthalates, commonly used as plasticizers and easily extracted from plastic material, can interfere with results and therefore compromise all the analytical process. Moreover, samples were not collected or stored in the presence of exhaust fumes.

Around 500g of soil is collected with a stainless steel spade and immediately wrapped with aluminium foil (Table 4.1). The wrapped portion of soil was placed inside of a plastic bag guaranteeing that the sample would not be in touch with the bag and the container is then labelled. Samples were kept cool (~4 ºC), in the dark and transported to the laboratory as soon as possible after collection.

Table 4.1 – Resume of sampling procedures for organics and inorganics.

Analysis	Sampling tool	Sampling depth	Amount of sample	Sample container	QC/QA	Max. Holding time
Inorganics analysis	Plastic spade	0-10cm 10-20cm	2-3 kg	Plastic bag	Standardized sampling site record; chain of custody record	6 months
Organic compounds analysis	Stainless steel spade	0-10cm	500g	Glass jar/ Teflon lined cap		Extract within 15 days/ Analyse within 40 days

4.3. Estarreja soil sampling maps

The digital cartography available was used to produce maps for sampling campaigns. Maps were produced on a GIS basis (ARCGIS 9.0®). These maps were used both to define sampling points (soil sampling protocols) and to present soil quality data. A GPS (Global Positioning System) was also used to input coordinates of sampled points on these maps.

Twenty six sites were sampled, at two depths, as it is shown in Figure 4.2. The land uses sampled were: ornamental gardens (OG), roadsides (RD), parks (PO) and agricultural (AG). As most roadsides in the urban area are subject of active planning and may also be considered ornamental gardens, another type of land use can be defined (Ornamental Garden/Roadsides (OG/RD). The number of samples collected for each one of the land uses is shown in Table 4.2. The initial choice of the sampling sites was followed, however, as sampling was accompanied by the Municipality staff it's was just possible to sample were it was allowed. Due to this limitation in two sites (site 1 and 8) only the first depth was collected, resulting in a total of 50 samples. Besides, in what concerns agricultural sites sampling was subjected to an authorization of the land owner. In Annex II it's presented a resume with the location and description of Estarreja soils sampling sites. Sampling campaign occurred during May of 2005.

Table 4.2 – Number of samples collected in Estarreja for each land use (see also Figure 4.2).

Land Use	nº of sites	Sites nº
OG	2	2,16
PO	2	13,14
OG/RD	5	3,7,8,9,12
RD	6	1,4,5,6,10,11
AG	11	15,17 to 26
Total	**26**	

4.4. Sample Pre-Treatment and Storage

4.4.1 Sample pre-treatment and storage for inorganics

The pre-treatment of samples was done in accordance to ISO method 11464:1994 (ISO, 1994a). This International Standard specifies the pre-treatment required for soil samples that are to be subjected to physical-chemical analysis and describes the following five types of pre-treatment of samples: drying, crushing, sieving, dividing and milling.

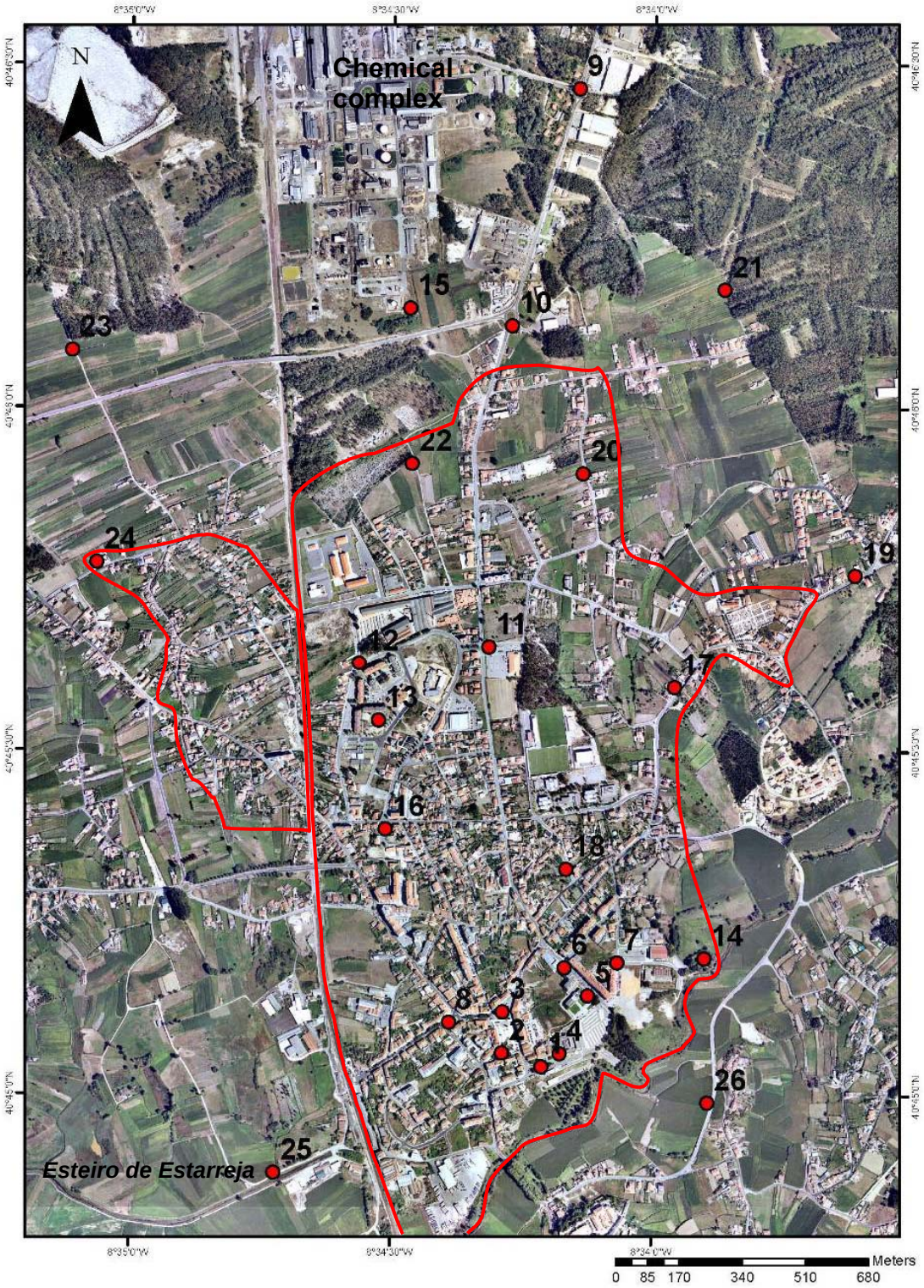


Figure 4.2 – Localization of sampling sites in Estarreja, the chemical complex and the urban area (1:10.000, from Série Ortofotocartográfica Nacional, IGP).

Soil samples were oven dried at 40 ºC as soon as arrived to laboratory to minimize microbial activity (mineralization). These samples were crushed while still damp and friable and again after drying, using a plastic hammer. Samples were thoroughly mixed and divided using the "cone-and-quarter" technique. The soil was sieved, with a nylon sieve, and the fraction smaller than 2 mm (10-mesh) was stored in the absence of light, for further analysis. Subsamples of 50g were taken from the fraction smaller than 2 mm, grinded (agate rings mill) and sieved to a fraction smaller than 150 µm. The maximum holding time until analysis should not exceed 6 months (Table 4.1).

4.4.2 Sample pre-treatment and storage for organic compounds

For organics sample pre-treatment has special cares (USEPA, 1996a) Samples were delivered to the laboratory as soon as possible after collection and dried in a cold and dark place for no longer then 2 days. Then a portion of each sample was sieved to <2 mm using a stainless steel sieve and frozen involved in aluminium foil. Samples should be extracted within 15 days of sampling (Table 4.1).

5. General characterization of Estarreja urban soils

5.1. Introduction

The following set of parameters was selected in order to obtain a general characterisation of Estarreja urban soils: soil pH in water (pH_W) and in $CaCl_2$ (pH_{Ca}), total C, N and H percentages, cation exchange capacity (CEC) and exchangeable bases, organic matter content by Loss on Ignition (LOI) and particle size distribution (PSD).

Soil pH can be used as an indicator of the acidity or alkalinity in the soil. It has different sources and in natural systems the pH is affected by the mineralogy, climate, and weathering. The pH of a soil affects the availability of both the essential elements such as phosphorous (P), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn), as well as non essential elements, such as aluminium (Al) or other potentially toxic metals (Zhou *et al.*, 2000).

Another important parameter to assess soils quality is soil organic matter (SOM) that comprises a variety of carbonaceous materials including humus, soil micro-organisms, plant and animal residues, coal, charcoal, coke and graphite (NEPC, 1999). Soil Organic Carbon (SOC) is the most abundant element of SOM and represents a significant component of the global carbon, being soil pool and processes important regulators of CO_2 in the atmosphere (Konen *et al.*, 2002). Other elements of SOM include nitrogen, oxygen, hydrogen, sulphur and phosphorous. The importance of SOM regards mainly due to its relevant role, together with pH, on trace metals mobility and bioavailability. In addition, SOM can interact strongly with many other organic compounds resulting in complexed species that shows altered reactivity (either enhanced or diminished), affecting, for example, the bioactivity, persistence and biodegrability of pesticides (Stevenson, 1982). It is also a source of hydrogen ions, through dissociation of acidic groups, and is therefore an environmental component which determines the bulk pH as well as the availability of protons.

Nutrients such as nitrogen (N), sulphur (S), calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) are originated from rock weathering and from atmospheric deposition. The amounts of nutrients supplied will therefore be dependent of local geology, rainfall and the proximity to the sea, sources of atmospheric pollution and atmospheric dust. The cations Ca, Mg, Na and K, are known as basic cations and they exist in soil primarily as exchangeable cations on the colloidal complex of the soil or they occur as simple inorganic salts (SPAC, 1999). The negative charges on clay and humus is balanced by charges on these cations and also by H^+ and aluminium ions (Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$) which are known as acidic cations (Wild, 1993). The ability of soil to yield

cations is known as Cation Exchange Capacity (CEC). This is, therefore, the measure of the readily exchangeable cations that neutralize negative charges of soil components, being important as source of nutrients (Ca, Mg, K and Na) and as buffer of pH.

Soil texture is also called particle or grain size distribution of particles constituting the soil (Boulding, 1994). The inorganic constituents of soil are sand, silt and clay, formed by weathering of parent rocks. Clay minerals together with SOM are particularly important from the environmental point of view due to their ability to adsorb ions, molecules and gases and therefore hold toxic pollutants.

Concluding, all these parameters are very important for assess soil function as they are responsible by providing nutrients to plants, contaminants mobility and water holding capacity. In addition, soil as sorptive characteristics, due to the electrical charges and large surface area of the clay mineral and humus (Wild, 1993). As a result, soil acts as buffer zone between the atmosphere and groundwater (Guvenç *et al.*, 2003), and in an urban context this property is extremely important due to the high atmospheric inputs.

5.2. Analytical methods and QC/QA procedures

5.2.1 pH_w and pH_{Ca}

Samples pH was determined according to the ISO method 10390:1994 (ISO, 1994b) using a glass electrode (WTW, Sentix 41) both, in a 1:5 (m/v) suspension of soil in water (pH_W) and in a solution of 0.01 mol/l calcium chloride (pH_{Ca}). Determination was undertaken in the < 2 mm soil fraction, for both surface and subsurface layer in a total of 50 samples.

A sub-sample of five grams of soil was taken to a centrifuge tube and it was added five times its volume of water or calcium chloride solution. Suspension was mixed using a mechanical shaker during 5 minutes, left for at least 2h, but no longer than 24 h. The pH determinations were performed twice, after 2 h and 20 h. Just before the determination of pH, the suspension was shaken thoroughly and the pH was measured in the settling suspension. The pH value was read after stabilization (pH value over a period of 5s does not vary more than 0.02 units). The pH-meter (WTW, mod. 538) was calibrated as prescribed in the manufacturer's manual, using buffer commercial solutions with pH 4.00 and 7.00.

5.2.2 Elemental Analysis (C, N and H)

Determinations were performed with an instrument for CHN microanalysis (LECO, CHNS-932) that measures carbon and hydrogen by means of individual, infrared detection systems while nitrogen is measured in a thermal conductivity detector system. Determinations are undertaken directly in sub-samples of around 1 g of soil milled and sieved to <150 μm, for both layers, being the total of samples analysed 50.

5.2.3 Organic matter (OM)

Total soil organic matter was estimated by measuring the weight loss due to the combustion (loss-on-ignition), upon heating at 430ºC according to Schumacher (2002). About ten grams of soil, sieved to <2 mm, were dried at 105 ºC for four hours to remove any residual water. Samples were then ashed at 430 ºC until constant weight (about 16 hours), and then allowed to cool in a dessicator. Each sample was weighed, prior and after heating, and the decrease in weight was calculated as a proportion of the initial weight and expressed as a percentage weight loss. Determinations were done in both surface and subsurface samples in a total of 50 samples.

5.2.4 Cation Exchange Capacity (CEC)

Potential CEC and exchangeable cations were determined in barium chloride solution buffered at pH = 8.1 using triethanolamine, following the principles of the ISO method 13536:1995 (ISO, 1995a). The principle of this method consists in an initial saturation of the soil with a buffered barium chloride solution, followed by an addition of a known excess of magnesium sulphate solution that precipitates all the barium present (in solution as well as adsorbed, in the form of highly insoluble barium sulphate) and the sites with exchangeable ions are then readily occupied by magnesium. The excess magnesium is then determined by titration and sodium, potassium, calcium and magnesium are determined in the barium chloride extract of the soil (exchangeable bases).

Two grams of air-dried soil (<2 mm fraction, surface layer) were weighted into a centrifuge tube and exactly 25 ml of the extraction solution was added to the sample. The extraction solution was prepared by dissolving 100 g of barium chloride dihydrate ($BaCl_2.2H_2O$) in about 800 ml of distilled water, adding 22.5 ml of triethanolamine $(HOCH_2CH_2)_3N$, adjusting the pH at 8.1+/-0.1 with HCl (1:1 v/v) and diluting to 1000 ml. The barium-ions exchange with cations present in the soil. Sample was then shaken for 3 min, rested for 5 min and shaken again for 3 min. The sample was centrifuged

(3000rpmX5min) and the supernatant was transferred to a volumetric flask, diluted to 100 ml, filtered (Whatman 54, Cat Nº1454, d=11cm, retention 20-25 mm, maximum ash per circle 0.05 mg) and preserved for analysis of the exchangeable cations (Na^+, K^+, Mg^{2+}, Ca^{2+}).

The precipitate was washed by adding 25ml of distilled water followed by centrifugation; after decantation of the supernatant to waste the precipitate was weighted to determine the water fraction present in the soil. The sample was then treated with 25 ml of 0.1M $MgSO_4$, shaken for 5 min and after centrifugation (3000rpmX5min) the supernatant was filtered. Exactly 10ml were titrated with EDTA 0.05N. For titration, 10ml of extract were transferred to an Erlenmeyer flask, approximately 10ml of the buffer solution NH_3aq/NH_4Cl (pH=10) and 20 ml of distilled water, were added. The indicator used was Eriochrome Black T added in an enough amount to produce wine-red colour. Solution was titrated with an EDTA standard solution to a clear blue colour. Calculations were performed by using the following formula:

$$CEC = \frac{1}{m_{sample}} x\left(250 - 10x\frac{N}{M}x(25 + B - A)\right)$$

where:
CEC = $cmol^+/kg$
m_{sample} =soil weight (g)
N=ml of EDTA used in the titration
M=ml of EDTA used in the blank
B-A= amount of water in the soil sample

5.2.5 Exchangeable Bases

Exchangeable bases were determined according to the ISO method 13536:1995 (ISO, 1995a). Sodium and potassium were measured in the acidified barium chloride-triethanolamine extract of soil samples by flame emission spectrometry (FES, Model GBC series 906 AA). The calibration series used ranged from 0.3 to 3 mg/l for Na and from 0.25 to 1.5 mg/l for K. Two millilitres of filtrate obtained (see point 5.2.4), 1 ml of HCl 1 mol/l and 7 ml of water were added to a test tube and mixed. The same was done to the blank extract. Sodium was determined at 589 nm and potassium at 766 nm using an air/propane flame.

Calcium and magnesium were determined in the acidified barium chloride triethanolamine extract by Flame Atomic Absorption Spectrometry (FAAS, Model GBC series 906 AA). The calibration series used ranged from 1 to 5 mg/l for both elements.

One millilitre of filtrate obtained (see point 5.2.4), 1 ml of HCl 1 mol/l and 8 ml of water were added to a tube and mixed. The same was done for the blank. Magnesium was determined at 285.2 nm using an oxidising (blue) air/acetylene flame and calcium at 422.7 nm using reducing air/acetylene flame. Calculations were performed by using the following formula:

$$[Exch] = \frac{(\lfloor Exch_{sample} \rfloor - [Exch_{blank}])xV_{sample}}{m_{sample}}$$

$$[Na_{Exch}] = \frac{0{,}435x(\lfloor Na_{sample} \rfloor - [Na_{blank}])}{m_{sample}} \qquad [K_{Exch}] = \frac{0{,}256\,x(\lfloor K_{sample} \rfloor - [K_{blank}])}{m_{sample}}$$

$$[Ca_{Exch}] = \frac{0{,}499x(\lfloor Ca_{sample} \rfloor - [Ca_{blank}])}{m_{sample}} \qquad [Mg_{Exch}] = \frac{0{,}823x(\lfloor Mg_{sample} \rfloor - [Mg_{blank}])}{m_{sample}}$$

where:

$[Na_{exch}]$, $[K_{exch}]$, $[Ca_{exch}]$, $[Mg_{exch}]$ = $cmol^{+}/kg$

$[Na_{sample}]$, $[K_{sample}]$, $[Ca_{sample}]$, $[Mg_{sample}]$ = concentration of elements in the sample (mg/ l)

$Na_{blank}]$, $[K_{blank}]$, $[Ca_{blank}]$, $[Mg_{blank}]$ = concentration of elements in the blank (mg/ l)

m_{sample} = soil weight (g)

5.2.6 Particle Size Distribution (PSD)

The determination of the PSD was performed through the analysis of main texture percentages: sand, silt and clay fractions. The determination of the sand fraction (2-0.075 mm) was obtained by dry sieving using the 75 µm ASTM standard sieve. Sand (0.075-0.050 mm), silt (0.050-0.002 mm) and clay (<0.002 mm) fractions were quantified by using the Micromeritics® Sedigraph 5100. Around 3 g of each sample (from <0.075 mm fraction) were accurately weighed and 0.16 mM sodium hexametaphosphate solution was added. The solution was fully dispersed using an ultrasonicator in order to disperse sample aggregates. The sedigraph was cleaned using distilled water and calibrated using the Spectromelt A 12 (66% di-Lithium tetraborate/34% Litium metaborate) (1.5 µm) reference material.

Each sample was then classified according to the percentages to the USDA classes by using the *Talwin 42*® classification software program. The classification was done only for SF layer in a total of 26 samples.

5.2.7 QC/QA Procedures

Method blanks were performed for all parameters, and at least one blank analysis was performed per process batch (10 samples). Precision was evaluated by calculating the variation between duplicate analyses in at least 10% of samples and results are shown in Figure 5.1. Repeatability of pH results, in separately prepared suspensions, satisfied the demands according to the ISO procedure (Table 5.1).

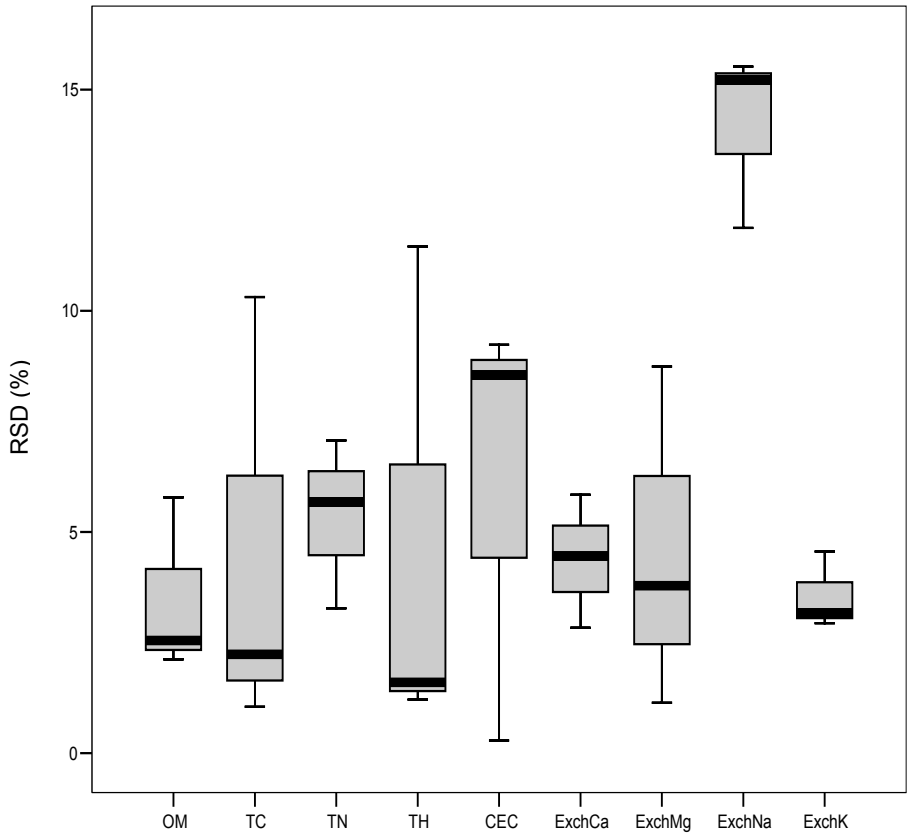


Figure 5.1 - Relative standard deviation (%) for the replicate analysis with the median and the interquartile range.

Table 5.1 – Acceptable variation between replicates according to pH range.

pH range	Acceptable variation (pH units)
$pH \leq 7$	0.15
$7 < pH < 7.50$	0.20
$7.50 \leq pH \leq 8.00$	0.30
$pH > 8.00$	0.40

For the determination of exchangeable cations, the instrument was calibrated with five acidified standards and a standard was analyzed every five samples to check for instrument drift. Standards were prepared in an acidified barium chloride-triethanolamine solution in order to reduce matrix effects. Detection limits were estimated from the calibration curve as the concentration giving a blank signal, plus three standard deviations of the blank and they were found to be 0.09 mg/l for Ca, 0.15 mg/l for Mg, 0.18 mg/l for Na and 0.06 mg/l for K.

Difficulties were found in obtain a complete validation data for all analytes due to the lack of suitable certified reference materials (CRM). However, whenever possible, CRM's were used. For Elemental Analysis (Total C, N) reference materials Eurovector E11036 and Eurovector E11037 were analysed in the same way as samples and recoveries were found to be 94 ± 9% (STDEV) for Total Carbon (TC) and 105 ± 8 % (STDEV) for Total Nitrogen (TN). For CEC the reference material used was the Lufa Speyer 2.2, a loamy sand soil with a CEC of 11 ± 1 mval/100 g and recoveries were found to be 94 ± 4% (STDEV). Table 5.2 lists the methods used, the number of samples analysed and the QC/QA procedures for each parameter.

Table 5.2 – Parameters, methods and QC/QA details.

Parameter	Procedure	Reference	QC/QA (3)	No. of samples
pH	1:5 (v/v) suspension in water, and 0.01 mol l^{-1} $CaCl_2$	ISO 10390:1994	R	50
CEC	0.01 mol l^{-1} $BaCl_2$; method of Bascomb at pH 8.1	(1); ISO 13536:1995	RM; R; B	26
ExchCa, Mg	Atomic absorption spectrometry (AAS)	ISO 13536:1995	R; B	26
ExchNa, K	Flame emission spectrometry (FES)	ISO 13536:1995	R; B	26
OM	Loss on ignition	(2)	R	50
Total C,N,H	Elemental analysis (C,H and N)	(1)	RM; R; B	50
PSD	Micromeritics® Sedigraph 5100	-	R	26

(1) University of Wageningen, 2000; (2) Schumacher, 2002; (3) R = replicates; RM = certified reference material; B = method blanks

5.3. Results and discussion

Descriptive statistics was initially performed on the data, histograms and box-plots were obtained and normality was tested by running the Kolmogorov-Smirnov test (SPSS 11.0) (results are shown in Annex III). As not all parameters follow a normal distribution, non-parametric statistics was used. Mann-Whitney Rank Sum Test was used for the comparisons between the two layers of urban soil, when applicable. All variables were then tested for correlations (for SF layer) and Principal Component Analysis (using STATISTICA® 6.0 software) was used to identify relationships between them, after log transformation of the original data. Finally, the influence of the land use was studied by using the Kruskal-Wallis One Way Analysis of Variance on Ranks test.

5.3.1 Characterization of physical and chemical properties of urban soils from Estarreja

5.3.1.1 Soil reaction of Estarreja samples

Summary statistics of pH determination for both, water and calcium chloride, in the two layers are shown in Table 5.3. For pH_w the median value in surface layer (SF) was 6.21, ranging from 4.83 to 7.16, and in subsurface layer (SB) it was 6.09, ranging from 4.53 to 8.15. The median value of pH_{Ca} for SF layer samples was 5.15, ranging from 4.08 to 6.88, and for SB layer this value was 4.91, ranging from 3.9 to 7.35. The results for pH_{Ca} is about 0.5 to 1.0 pH units lower than for water extract, due to the higher concentration of H^+ ions in solution as a result of ion exchange with Ca^{2+} in soil particles. This method gives more precise values, being recommended where the salt content may influence the pH value. Nevertheless, just for classification purposes of the pH_w in both layers, USDA [w_{13}] classes will be used for setting the acidity and alkalinity limits as shown in Figure 5.2.

Table 5.3 –Summary statistics for pH (water and $CaCl_2$) in surface (SF) and subsurface (SB) layers.

	pH_w		pH_{Ca}	
	SF	**SB**	**SF**	**SB**
mean	6.13	6.15	5.21	5.19
median	6.21	6.09	5.15	4.91
st. dev	0.56	0.88	0.69	0.95
max	7.16	8.15	6.88	7.35
min	4.83	4.53	4.08	3.90
range	2.33	3.62	2.80	3.45
RSD (%)	9.1	14.3	13.2	18.3

Differences between sample depths were observed for some individual samples but no general pattern was found, and when performing the Mann-Whitney Rank Sum Test differences were not statistical significant. Both, the lowest (sample 15.AG) and the highest value (sample 6.RD) of pH were found in the SB layer. In both cases the difference between the two layers is quite significant, yet in the second case the difference is even greater.

According to the USDA classification soils having a pH less than 6.6 are classified as acidic, when is above 7.3 are alkaline and when between those values are neutral soils. From Figure 5.2 and Table 5.3 its possible to conclude that Estarreja soils are, in what concerns the median value, classified as slightly acid (6.1<pH<6.5), with most of the samples bellow the acidity upper limit. Following the USDA classification (Figure 5.3 and Figure 5.4), samples 18.AG (SF and SB) and 15.AG.SB are considered very strongly acid (4.5<pH<5.0), and samples 22.AG (SF and SB) and 9.OG/RD.SF are considered strongly acid (5.1<pH<5.5). On the other hand, samples 11.RD.SB and 26.AG.SB were classified as slightly alkaline (7.4<pH<7.8) and sample 6.RD.SB was considered moderately alkaline (7.9<pH<8.4).

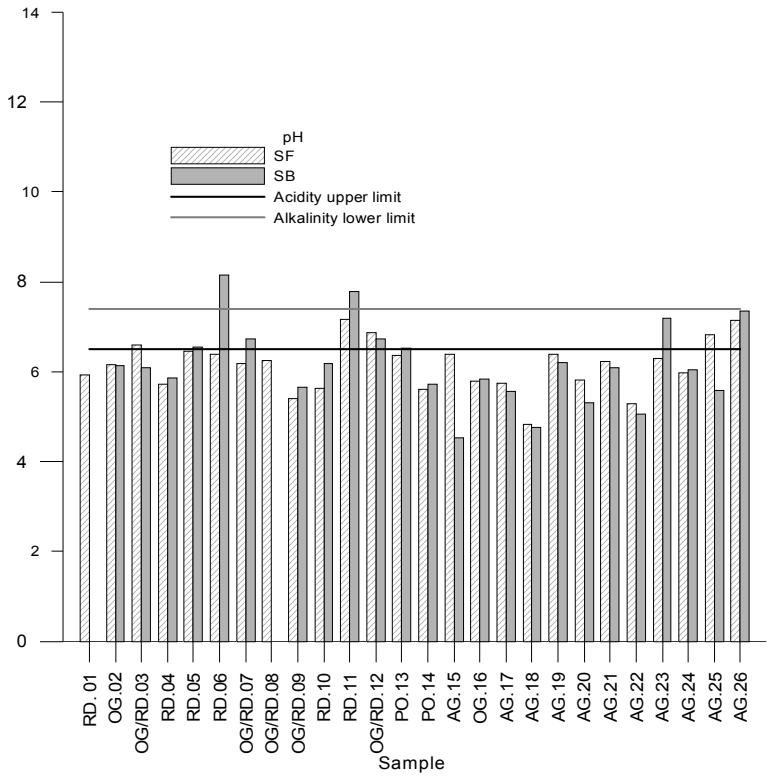


Figure 5.2 - Results pH_w for Estarreja samples in both layers and both acidity and alkalinity limits (as defined by USDA [w_{13}]).

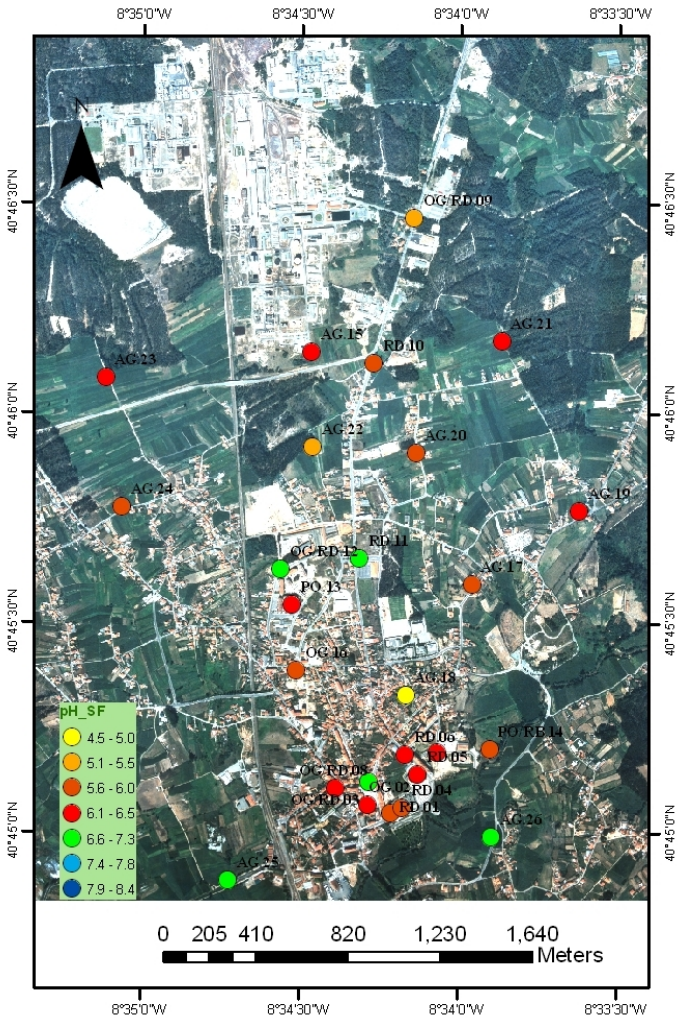


Figure 5.3 – Spatial distribution of the pH_w for each sample in SF layer, according to USDA classes [w_{13}].

Although non-natural soil alkalinity has been reported in urban soils, due to the release of calcareous solutions from building wastes (Jim, 1998), this was not verified in Estarreja. The main reason for the acidity reported in Estarreja soils is likely to be the soil type, however other factors such as atmospheric inputs from industry (especially HCl, HNO_3, NH_3, NH_4^+), gases from atmosphere (SO_2, CO_2), deposit of aerosols and the acidic rain may have some importance (Wild, 1993). Values of SO_2 measured in the monitoring station of Estarreja (see point 3.4) are not very high (bellow the maximum value of 125 $\mu g/m^3$ daily base, with very few days exceeding this value) and the same was observed for NO_2. However, as it is possible to observe in Table 3.4, the industry around Estarreja releases several tons of SO_x and NO_x. In addition, pH in rainwater for Aveiro region can be considered acid (about 5.4), being found values as low as 5.0 (Condesso de Melo, 2002).

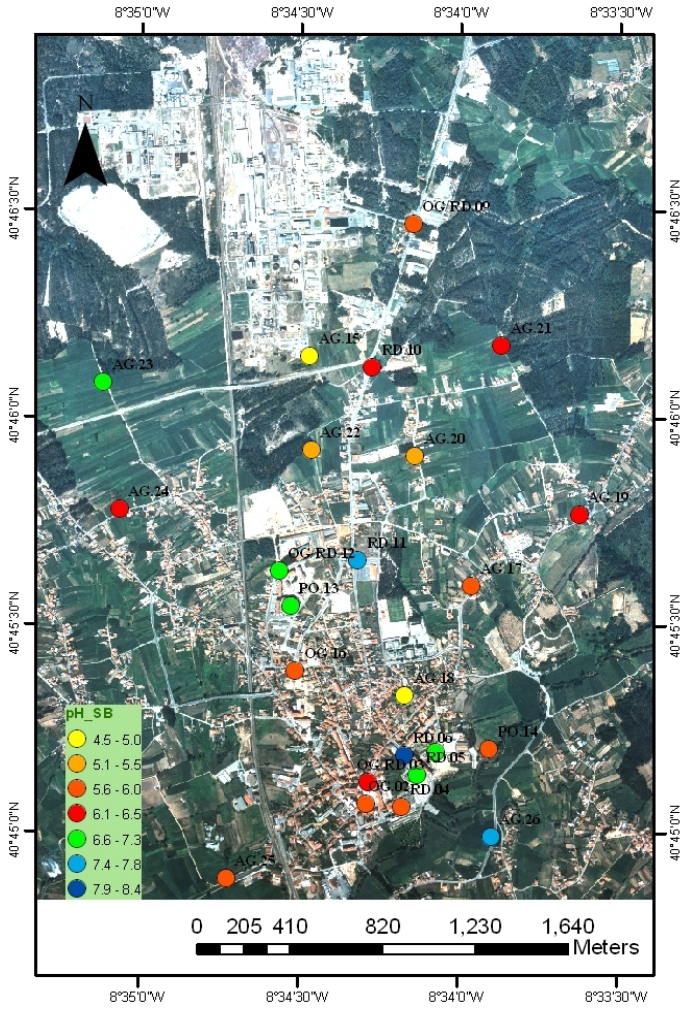


Figure 5.4 – Spatial distribution of the pH_w for each sample in SB layer, according to USDA classes [w_{13}].

A pH range of 6 to 7 is generally most favourable for plant growth due to availability of nutrients (USDA - [w_{13}]). These values were not observed in all Estarreja samples being either too low or too high. Samples 9.OG/RD.SF, 15.AG.SB, 18.AG, 20.AG.SB and 22.AG.SF (pH<5.5) or samples 6.RD.SB and 11.RD.SB (pH>7.8) will show problems on nutrients availability either due to their high or low solubility. Another important effect of pH is the solubility of potentially toxic metals under acid conditions which can move downward with water through the soil, in some cases moving to aquifers or surface streams.

5.3.1.2 Characterization of SOM and Total C, N and H in Estarreja soils

OM was estimated by loss-on-ignition and results for each individual sample are shown in Table 5.4, together with results of total C, N and H. Figure 5.5 shows the box plots,

including the outliers and extreme values, for these parameters. For surface (SF) samples the median value of OM was 4.4 %, ranging from 1.8 to 8.9% and for subsurface (SB) samples the median value was 3.4%, ranging from 1.6 to 6.2% (Table 5.5). Therefore, considering the median, soils from SF layer can be considered as having a high content of OM (>4%) and soils from SB layer have a medium content (4<OM%<2) (Boulding, 1994).

The difference between the two layers was found to be statistically different (Mann-Whitney Rank Sum Test, P=0.006), being the SF layer normally enriched in OM. In Figure 5.5 and Figure 5.6 it is possible to observe these differences between layers and between sites, as well as samples that are above and bellow the median value. The enrichment factor of OM, the ratio between OM (%) in SF and SB (EF=SF/SB), was calculated for each sample and results (Table 5.4) shows that this ratio is equal or higher than one for all samples, reaching values as high as 2.7 (sample 6.RD).

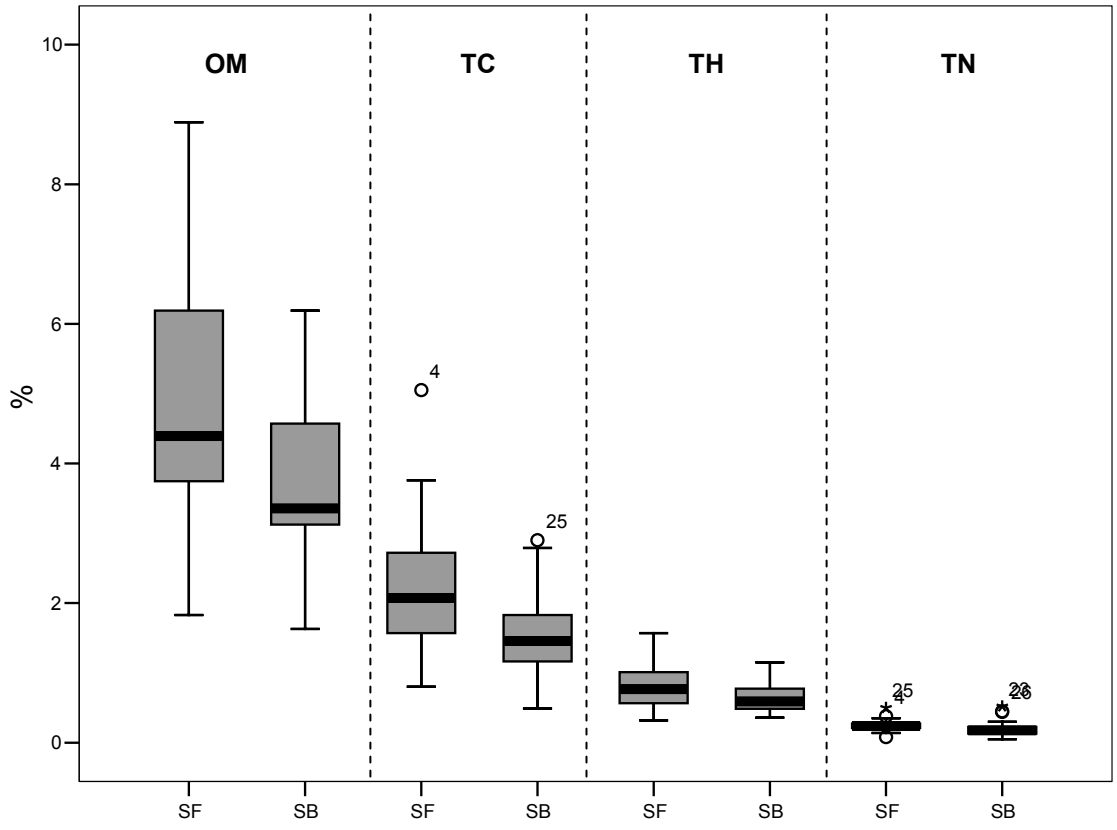


Figure 5.5 – Box plots of OM, TC, TH, TN in both surfaces, with the median, the interquartile range, the outliers (between 1.5 - 3 box lengths) and extreme values (more than 3 box lengths).

Table 5.4 – Values of Total C, N, H, ratio C/N, OM (%), enrichment factor (EF) and OC/OM for Estarreja samples.

Sample	Total Carbon %		Total Nitrogen %		Total Hydrogen %		Ratio C/N		OM (%)		EF	OC/OM	
	SF	SB	SF	SB	SF	SB	SF	SB	SF	SB		SF	SB
01.RD	2.69	-	0.24	-	0.99	-	11.2	-	6.12	-	-	44.0	-
04.RD	5.05	2.18	0.38	0.17	1.32	0.67	13.0	12.8	7.32	5.42	1.35	69.0	40.2
05.RD	2.24	1.02	0.25	0.13	0.71	0.49	8.96	7.85	3.74	2.44	1.53	59.9	41.8
06.RD	3.58	1.01	0.29	0.10	1.27	0.60	12.3	10.1	8.35	3.08	2.71	42.9	32.8
10.RD	2.22	1.45	0.23	0.18	1.11	0.91	9.65	8.06	6.04	4.43	1.36	36.8	32.7
11.RD	0.80	0.49	0.08	0.05	0.32	0.36	10.0	9.80	1.83	1.63	1.12	43.7	30.1
07.OG/RD	2.70	0.88	0.26	0.08	1.09	0.42	10.4	11.0	3.86	2.38	1.62	69.9	37.0
08.OG/RD	1.45	-	0.17	-	0.91	-	8.53	-	4.22	-	-	34.4	-
09.OG/RD	1.31	1.35	0.14	0.15	0.78	0.83	9.36	9.00	3.92	3.32	1.18	33.4	40.7
12.OG/RD	2.09	1.03	0.21	0.11	0.87	0.53	9.95	9.36	3.75	2.91	1.29	55.7	35.4
03.OG/RD	3.56	1.46	0.35	0.13	0.93	0.46	10.2	11.2	7.23	2.83	2.55	49.2	51.6
02.OG	2.74	2.08	0.25	0.20	0.83	0.75	11.0	10.4	6.34	5.60	1.13	43.2	37.1
16.OG	1.41	1.15	0.16	0.15	0.82	0.63	8.81	7.67	4.24	3.39	1.25	33.3	33.9
13.PO	2.17	1.47	0.21	0.15	0.76	0.62	10.3	9.80	5.50	3.87	1.42	39.5	38.0
14.PO	3.56	1.85	0.32	0.22	1.57	1.08	11.1	8.41	8.89	5.66	1.57	40.0	32.7
15.AG	2.06	2.79	0.17	0.30	0.55	0.80	12.1	9.30	4.64	4.71	0.99	44.4	59.2
17.AG	1.82	1.75	0.21	0.20	0.65	0.68	8.67	8.75	4.54	4.76	0.95	40.1	36.8
18.AG	1.46	1.53	0.16	0.14	0.45	0.48	9.13	10.9	3.19	3.42	0.93	45.8	44.7
19.AG	2.30	1.18	0.25	0.13	0.73	0.52	9.20	9.08	4.81	3.64	1.32	47.8	32.4
20.AG	2.04	1.97	0.24	0.26	0.51	0.58	8.50	7.58	4.59	3.27	1.40	44.4	60.2
21.AG	2.03	1.81	0.21	0.20	0.58	0.55	9.67	9.05	4.08	4.27	0.96	49.8	42.4
22.AG	1.90	1.38	0.24	0.19	0.60	0.49	7.92	7.26	4.05	3.19	1.27	46.9	43.3
23.AG	1.68	1.38	0.25	0.52	0.48	0.42	6.72	2.65	3.54	3.24	1.09	47.5	42.6
24.AG	1.41	1.23	0.23	0.23	0.53	0.46	6.13	5.35	3.53	3.17	1.11	39.9	38.8
25.AG	3.76	2.90	0.50	0.44	1.44	1.15	7.52	6.59	8.52	6.19	1.38	44.1	46.8
26.AG	1.37	1.78	0.31	0.45	0.77	0.95	4.42	3.96	3.22	3.32	0.97	42.5	53.6

In what concerns the percentages of total C, N and H, the median concentration was found to be higher in the SF layer than in the SB for the three parameters (Table 5.5), being the difference between the two layers statistically significant for all cases (Mann-Whitney Rank Sum Test, P=0.002 for TC, P=0.014 for TN and P=0.019 for TH). These differences between layers and dispersion of results are displayed in Figure 5.5.

Table 5.5 - Summary statistics for TC, TN, TH and OM (all values in %).

	Total Carbon		Total Nitrogen		Total Hydrogen		OM	
	SF	**SB**	**SF**	**SB**	**SF**	**SB**	**SF**	**SB**
mean	2.28	1.55	0.24	0.20	0.83	0.64	5.00	3.76
median	2.08	1.46	0.24	0.18	0.78	0.59	4.39	3.36
st. dev	0.96	0.57	0.08	0.12	0.32	0.21	1.83	1.15
max	5.05	2.90	0.50	0.52	1.57	1.15	8.89	6.19
min	0.80	0.49	0.08	0.05	0.32	0.36	1.83	1.63
range	4.25	2.41	0.42	0.47	1.25	0.79	7.06	4.56
RSD (%)	42.1	36.8	33.3	60.0	38.6	32.8	5.00	3.76

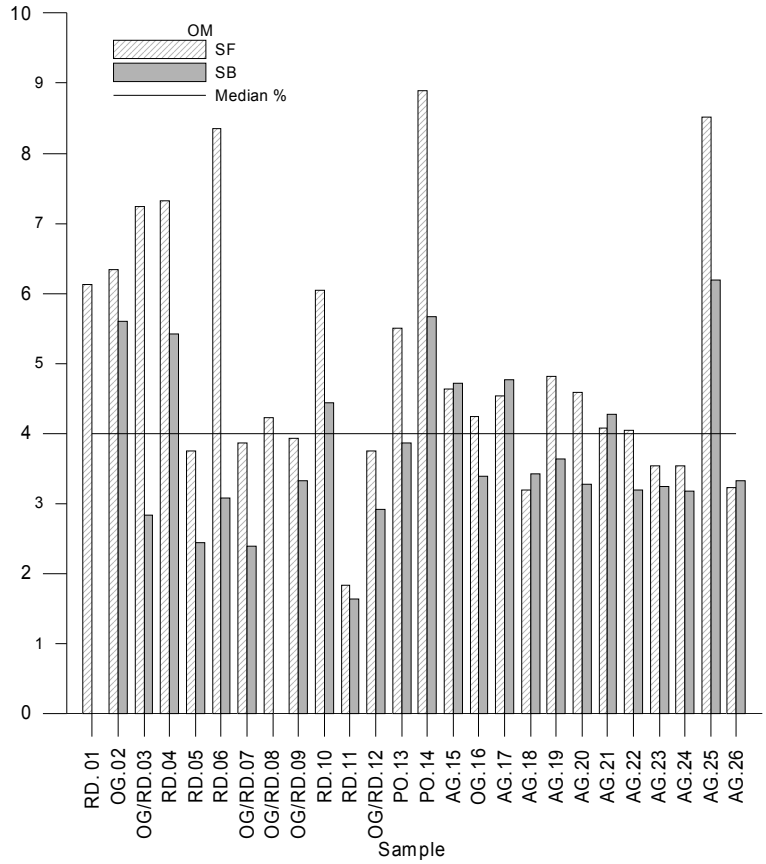


Figure 5.6 - % of OM, in each layer, for each sampling point and the median value (considering all results).

LOI is a proxy measurement of organic matter, being the ashes that remain inorganic particles. The method adopted is classified by EPA as semi-quantitative (Schumacker, 2002). One of the problems of this method is the loss of carbonate carbon, to which carbonate soils are especially prone. Estarreja soils are not carbonated soils and in addition in soils with a pH_{Ca} less than 6.5 the presence of carbonates is unlikely (ISO, 1995b). Moreover, as temperature was kept below 440 ºC, even if inorganic carbonates were present they would not be decomposed. In what concerns the loss of structural water from clay minerals, that can result in an overestimation of OM content (Schumacker, 2002), it is not expected to interfere with results as Estarreja samples have low clay content.

The calculation of the soils organic carbon (OC) from LOI is widely based on the assumption that a constant fraction of the dry LOI is OC (58%). However the use of such universal conversion factor may be linked to redundancy arising from various sources of error related to the nature or age of SOM (Westman *et al.*, 2006). Estarreja soils are not carbonated and therefore TC can be considered equal to OC. Pearson correlation between SOM and TC, in SF layer, was found to be 0.862 ($p<0.05$), meaning that the proportion of OC in SOM increases with the quantity of SOM (OC=0.46*SOM). For SB layer results were quite similar (Pearson correlation of 0.862 and the equation was OC=0.41*SOM). These results are in accordance with the range found by Westman *et al.* (2006) for podzolic soils (from 0.33 to 0.59). Values of OC in SOM above 55%, common in old soils (Craft *et al.*, 1991), were found in samples 4.RD.SF, 5RD.SF, 7.OG/RD.SF and sample 12.OG/RD.SF (Table 5.4), which are roadsides covered with grass and known to be old. Values around 40%, which are typical of young soils with recently deposited plant material (Craft *et al.*, 1991), were found mainly in ornamental gardens and agricultural sites.

For Estarreja samples the median value of C/N ratio was 9.5 for SF layer and 9.0 for SB layer. Values are close to 10 indicating the presence of humus, with the lowest value (Table 5.4) found in sample 23.AG.SB (C/N=2.7) and the highest in sample 4.RD.SF (C/N=13.3). Values of about 10 are common for neutral well-drained agricultural soils through the world, but under wetter or more poorly drained conditions and under acid conditions this ratio is higher and may be as high as 17 (Russel, 1973).

The median percentage of total N (0.2%) is not high, being bellow the normal values in warm humid regions of 0.3% (Tan, 1994), still some higher values were found (0.5% in sample 25.AG). These low results are in accordance with rainfall concentrations, in which

annual average values of $N\text{-}NO_3$ are reported to be 0.124 mg/l and 0.104 mg/l in two stations near Estarreja, Aveiro and Albergaria respectively (Condesso de Melo, 2002). Moreover, proximity to the sea, sources of atmospheric pollution and atmospheric dust (Wild, 1993) don't seem to have some influence on the results as it should be expected.

5.3.1.3 The CEC and exchangeable bases of Estarreja soils

CEC is a reversible process in which one mol of cation charge in solution replaces 1 mol of cation charge on the exchanger and it is measured in centimols per kilogram (cmol/kg) or in milliequivalents per 100 grams (meq/100g). The median value of 11.1 cmol/kg (Table 5.6) can be considered relatively low, according to EPA classes, that defines low values the ones bellow 12 cmol/kg and medium values between 12 and 20 cmol/kg (Boulding, 1994). Considering the type of soil and the low pH values obtained for Estarreja samples, the CEC values obtained are according to what was expected. Still, in the study area values ranged from 5.3 to 19.4 cmol/kg (Table 5.6 and Figure 5.7). The lowest value was found in sample 11.RD.SF and the highest one in sample 14.PO.SF, following the same pattern of OM.

Results of the exchangeable cations, including the summary statistics are shown in Table 5.6. Of the four cations Ca is the most abundant, with a median value of 4.8 cmol/kg, followed by Mg (4.2 cmol/kg), then Na (0.5 cmol/kg) and at last, K with a median value of 0.1 cmol/kg and most of samples below detection limit. This difference between concentrations of exchangeable cations in Estarreja samples can be easily observed in Figure 5.7 and Figure 5.8, with the former showing the concentration of all four cations in each sample.

The typical exchangeable cations distribution in well-farmed temperate soils is 80% of Ca, 15 % of Mg and Na and K together rarely more than 5% (Russel, 1973). In Estarreja, as it's possible to observe in Figure 5.8, only sample 8.OG/RD is near these percentages (67%, 28% and 5%). Samples 2.OG, 5.RD, 7.OG/RD, 9.OG/RD, 14.PO, 16.OG, 21.AG, 22.AG and 26.AG have more exchangeable Mg than Ca, what is typical in soils derived from magnesium-rich rocks or natural leached non-calcareous soils. Sample 25 showed very high contents of both CaExch and MgExch, being also the sample with highest CEC. The composition of exchangeable cations (EC) depends on the composition of weatherable minerals in the soil and their rate of weathering, mineral composition of the rain water, dust blown, addition of waste, fertilizer applications, aerosols deposition and irrigation (Russel, 1973; Yong *et al.*, 1992).

Table 5.6 – Values of CEC, exchangeable cations, exchangeable acidity and % base saturation for Estarreja samples.

Samples	CEC (cmol/kg)	[CaExch] (cmol/kg)	[MgExch] (cmol/kg)	[NaExch] (cmol/kg)	[KExch] (cmol/kg)	ExchAcidity (cmol H^+/kg)	%Base Saturation
01.RD	11.3	5.74	4.85	0.52	0.10	0.04	99.6
04.RD	17.2	5.50	4.48	0.56	0.11	6.59	61.8
05.RD	8.65	6.65	7.44	0.35	0.11	-	-
06.RD	18.9	6.40	4.97	0.34	BDL	7.20	61.9
10.RD	13.3	4.22	5.46	1.93	0.11	1.57	88.2
11.RD	4.47	2.80	1.91	0.32	BDL	0.24	95.6
03.OG/RD	16.3	10.2	8.00	0.33	BDL	-	-
07.OG/RD	8.26	5.22	8.53	0.45	0.31	-	-
08.OG/RD	11.7	3.34	1.38	0.25	BDL	6.75	42.4
09.OG/RD	7.60	1.44	0.58	2.59	BDL	2.99	60.7
12.OG/RD	9.69	5.96	5.60	1.51	0.28	-	-
02.OG	16.8	6.52	7.00	0.41	BDL	2.87	82.9
16.OG	9.35	2.16	2.26	0.46	0.11	4.36	53.4
13.PO	13.0	6.74	3.69	0.74	0.10	1.69	87.0
14.PO	19.4	4.83	6.36	0.64	0.11	7.44	61.6
15.AG	14.5	4.45	2.14	0.44	0.15	7.28	49.7
17.AG	11.5	3.17	2.91	0.55	0.20	4.69	59.3
18.AG	9.60	1.76	1.91	1.71	BDL	4.22	56.0
19.AG	11.1	7.72	5.73	0.51	0.33	-	-
20.AG	7.83	4.78	3.85	1.17	0.10	--	-
21.AG	8.85	1.40	2.85	0.25	BDL	4.35	50.9
22.AG	9.02	0.77	1.42	0.26	0.14	6.43	28.7
23.AG	8.75	4.32	3.17	0.61	0.23	0.42	95.2
24.AG	9.87	2.75	2.78	1.11	BDL	3.23	67.3
25.AG	19.2	16.6	10.9	0.93	0.19	-	-
26.AG	11.0	7.36	7.81	0.56	0.58	-	-
mean	11.8	5.11	4.54	0.75	0.19	4.02	66.8
median	11.1	4.81	4.17	0.54	0.14	4.29	61.7
st. dev	3.96	3.26	2.63	0.59	0.13	2.55	20.1
max	19.4	16.6	10.9	2.59	0.58	7.44	99.6
min	5.27	0.77	0.58	0.25	0.10	0.04	28.7
range	14.1	15.9	10.3	2.34	0.48	7.40	70.9
RSD (%)	33.4	63.8	57.9	78.7	68.4	63.4	30.2

BDL= Below detection limit

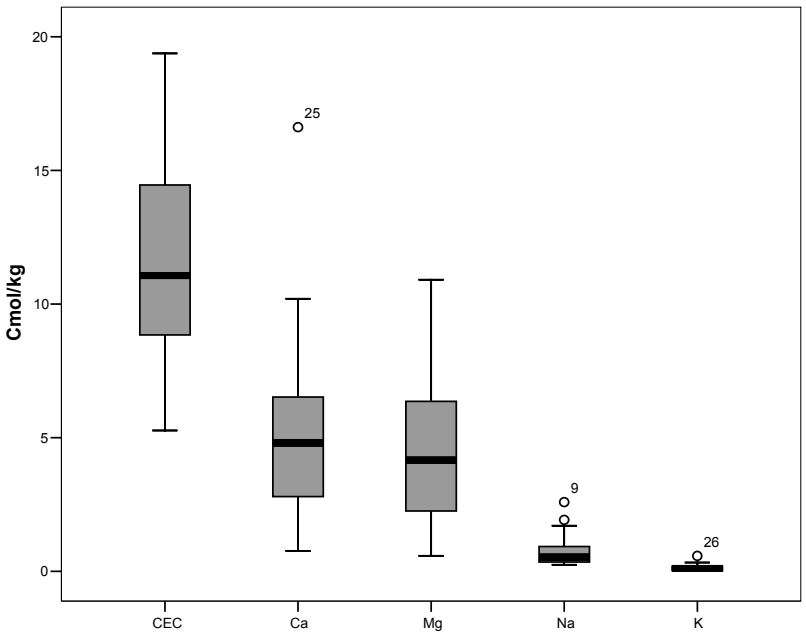


Figure 5.7 - Box plots for CEC, exchangeable Ca, Mg, Na and K. with the median, the interquartile range, and the outliers (between 1.5 - 3 box lengths).

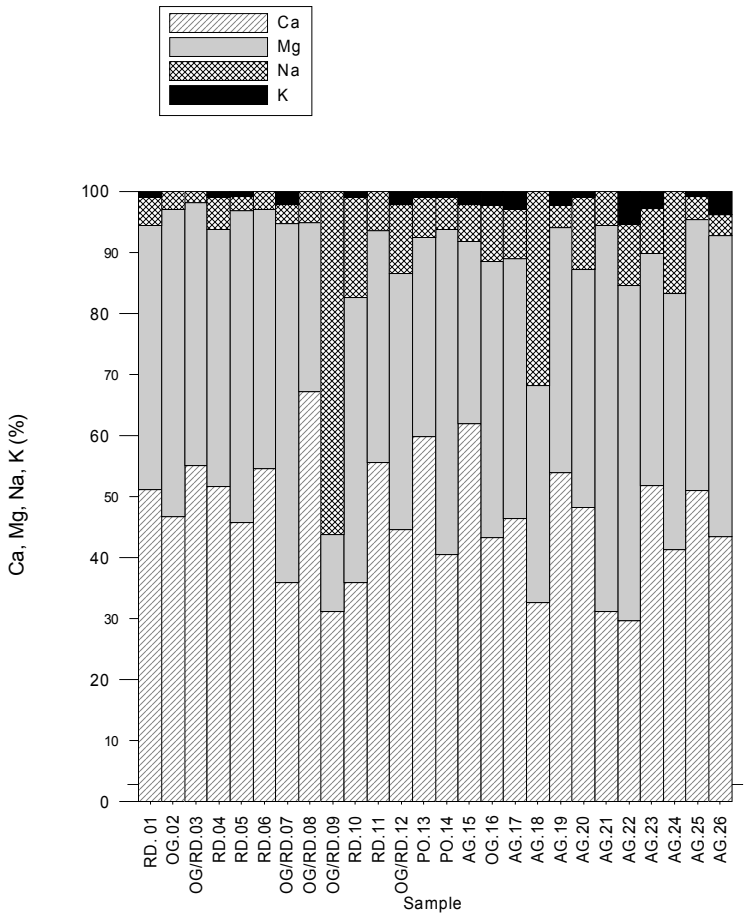


Figure 5.8 – Percentages of the exchangeable cations (Ca, Mg, Na, K) in each sample.

Concentration of exchangeable Na is high in some Estarreja samples, being the highest value found in sample 9.OG/RD (2.59 cmol/kg). Some samples showed an exchangeable Na percentage (% of total exchangeable base content) above 15%, the threshold above which soils are considered to be sodium-affected (sodic) (Ellis & Mellor, 1995). This may be happening in samples 9.OG/RD (56% of Na), 10.RD (16.5% of Na), 18.AG (31.2% of Na) and 24.AG (16.7% of Na). Na is toxic to many species and it has a deleterious effect on soil structure, because aggregation of clay particles does not occur and therefore soil particles are dispersed giving adverse physical conditions (Wild, 1993). One explanation for these high values may be the high concentration of Na in rainwater, as the level of Na can be controlled by this factor (Russel, 1973). The local rainfall has annual averaged Na/Cl ratios of 1.21, close to the characteristic value for the seawater 0.85, and reflecting marine aerosol (Condesso de Melo *et al.*, 2002). The relative high percentage of Mg found in samples may also be an indication of a marine influence. Results may also be affected by the parent material (sand dunes) or can be influenced by free sodium salts. Data about salinity should have been measured from the electrical conductivity, in order to determine how far this parameter is influencing the results.

In calcareous soils, the sum of the cations (Σ Ca, Mg, K, and Na) is invariable equal to CEC since any deficit of the cations on the exchanger can be made up by Ca^{2+} ions from the dissolution of $CaCO_3$. In non-calcareous soil, which is the case of Estarreja, this sum is frequently lower than the CEC, being the difference referred as exchange acidity (in cmol H^+/kg soil). The exchange acidity is mainly due to Al^{3+} ions that can be displaced by leaching with strong salt solution. In some cases the sum of exchangeable cations in Estarreja soils was found to be higher than the CEC, meaning that probably soluble salts were present in soil samples. Therefore, a pre-wash with aqueous ethanol or glycerol should have been made to remove soluble salts. As a result, in these samples (3.OG/RD, 5.RD, 7.OG/RD, 12OG/RD, 19.AG, 20.AG, 25.AG and 26.AG) the percent of base saturation (%BS = ΣEC/CEC) is higher than 100. This way, %BS and exchangeable acidity was calculated for all samples except these ones (Table 5.6). Considering these results, the lowest value of %BS was found in sample 22.AG (28.7%) and the highest one in sample 11.OG/RD (95.6%). For exchange acidity results ranged from 0.4 cmol H^+/kg, in sample 23.AG, to 7.4 cmol H^+/kg in sample 14.PO.

5.3.2 Estarreja soil's texture

The determination of the particle size distribution (PSD) of Estarreja surface samples was performed and the main texture percentages were obtained: sand, silt and clay fractions.

Figure 5.9 shows that the dominant fraction is sand, followed by silt and with a very low percentage the clay. Figure 5.10 shows the percentages of each fraction for individual samples. Samples are predominantly coarse textured with sand particles exceeding 70% by weight in 13 samples. The highest total fine fraction content was 58% for sample 14.PO (silt loam) and the lowest was 14% for sample 11.RD (sand). All other samples are classified as sandy loam or loamy sand.

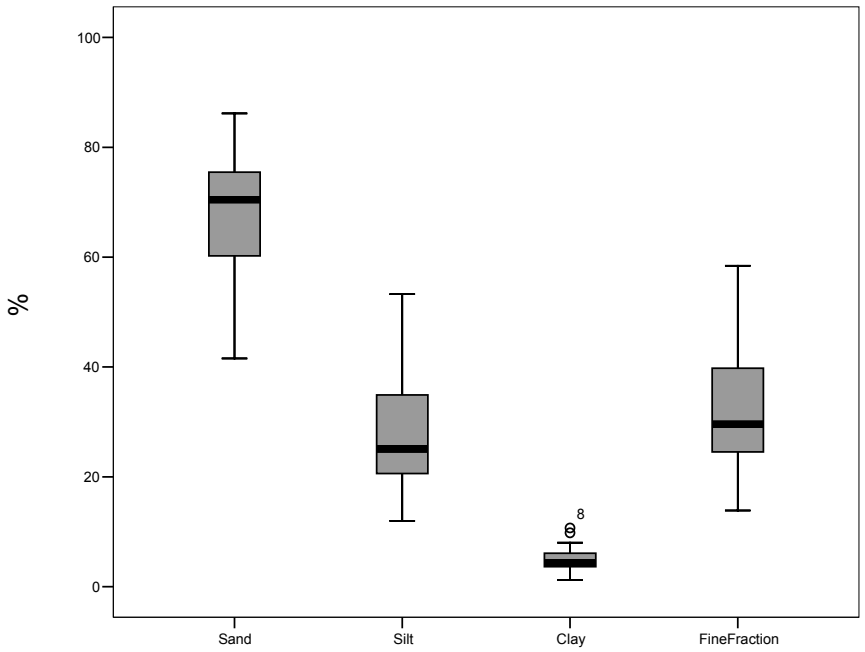


Figure 5.9 – Box plot of the percentages of sand, silt, clay and the total fine fraction, with the median, the 25th and 75th percentile and the outliers (outside the 5th and the 95th percentile).

Samples were classified according to the percentages of the USDA soil texture classes (USDA - [w_{13}]). This was achieved using the Talwin 42® classification program which classifies the texture class of each sample according to the respective sand and fine fraction percentages. Figure 5.11 shows all 26 Estarreja surface samples, plotted in the in the triangular diagram according with the USDA classification system. Although most of the samples fell in the same texture class, it is possible to distinguish the four classes: sand, sandy loam, loamy sand and silt loam. The majority of Estarreja samples (16 samples) are classified as sandy loam, eight samples are classified as loamy sand, one as silt loam and one as sandy.

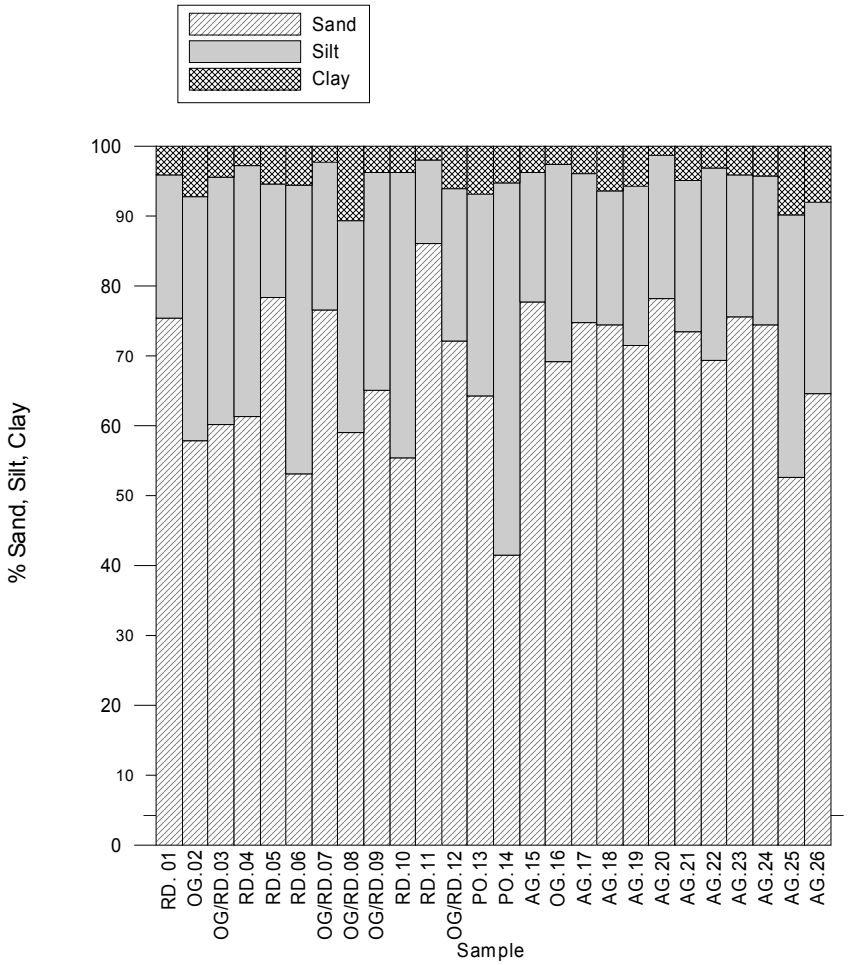


Figure 5.10 – Percentages of each fraction in individual samples.

The results of PSD in Estarreja samples can be explained by the local geology and soil type. One of the problems associated with the light texture of soils is that the shortage of fine particles limits the formation of a strong soil structure due to the lack of aggregating agents and bridging materials between coarse grains. Texture is also responsible for the fraction of available water and in this case soils are very permeable allowing water infiltration and drainage. According to USDA, the fraction of available water is less than 0.1 for sands, loamy sands and sandy loams in which the sand is not dominated by very fine sand. For loamy sands and sandy loams in which very fine sand is the dominant sand fraction, and loams, clay loam, sandy clay loam and sandy clay is 0.1 – 10.15.

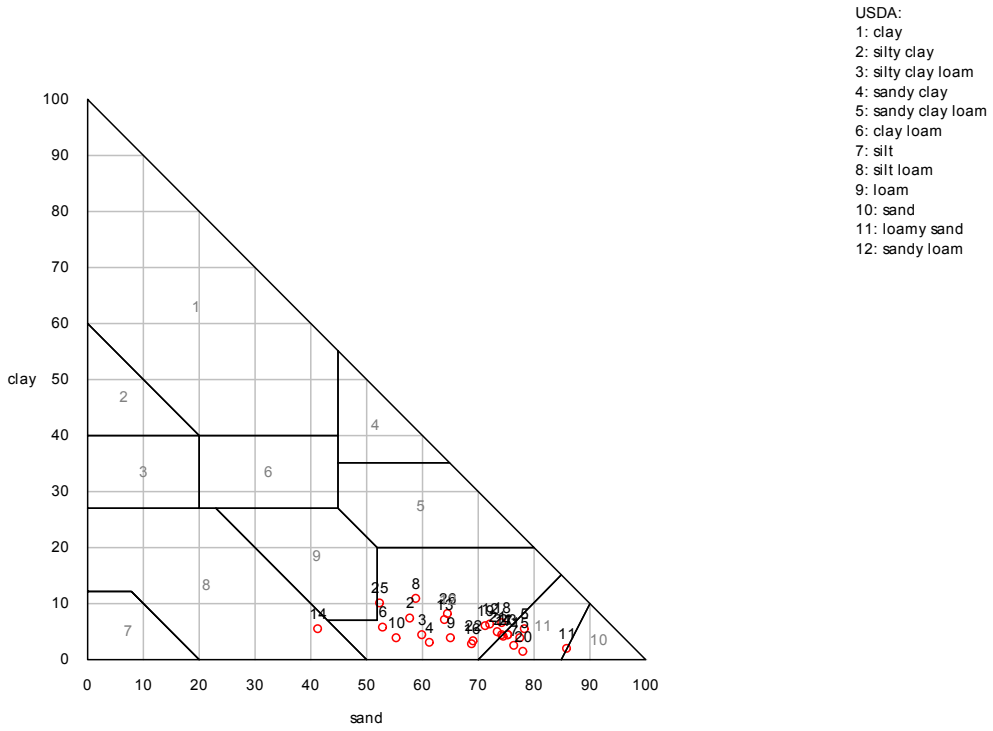


Figure 5.11 - Texture chart for the surface Estarreja samples plotted according to the USDA classification system using the Talwin42® program.

5.3.3 Application of multivariated analysis to Estarreja soil's general parameters

Principal Component Analysis (PCA) was performed in order to identify relationships between the studied variables. Therefore, eigenvalues extracted are presented in Figure 5.12. The first four factors were considered as they have eigenvalues higher than unit and explain 83% of the data, being only the first one responsible for 46.7%. Table 5.7 shows the factor loadings (with the ones higher than 0.5 marked in bold) the percentage of explained variance and the cumulative explained variance.

By observing Table 5.7 and Figure 5.13, were the projection of the first factorial plan is represented, its possible to conclude that the first factor is loaded by the variables OM, CEC, TH, TC, TN, silt, MgExch and CaExch in opposition to sand. The second factor is loaded by the pH followed by the KExch. However CaExch and MgExch are explained by both factors. The factorial plan defined by the first two factors contains 63.8% of the total information of the correlation matrix, explaining 11 of the 14 variables.

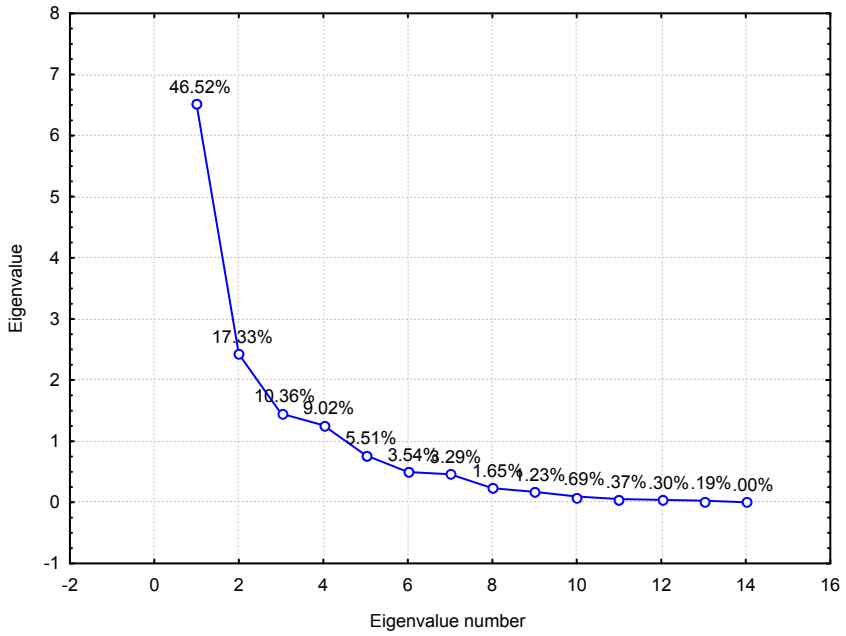


Figure 5.12 – Scree plot of the 14 eigenvalues extracted.

Table 5.7 – Factor loadings between all parameters determined and the first four factors of the analysis, eigenvalues and percent of variance.

Variable	Factor 1	Factor 2	Factor 3	Factor 4
pHCa	0.110692	**0.790137**	0.166500	-0.404762
CEC	**0.916022**	-0.141257	-0.002100	-0.156240
TC	**0.888571**	-0.045264	0.321656	0.211022
TN	**0.841742**	0.241462	-0.114543	0.205695
TH	**0.892331**	-0.122632	-0.034484	0.079005
C/N	0.271636	-0.451435	**0.742769**	0.055614
% Sand	**-0.813813**	0.340423	0.262543	0.208211
% Silt	**0.811468**	-0.411309	-0.261042	-0.068183
%clay	0.423054	0.123391	-0.474850	**-0.601189**
[CaExch]	**0.669846**	**0.588304**	0.103597	-0.007151
[MgExch]	**0.674866**	**0.596912**	0.131916	0.145810
[NaExch]	-0.032656	-0.216481	**-0.555143**	**0.533136**
[Kexch]	0.165960	**0.622913**	-0.203970	**0.508730**
% OM	**0.927476**	-0.256389	0.115131	0.064848
Eigenvalue	6.512183	2.426768	1.450936	1.262405
% Expl. Variance	46.51559	17.33406	10.36383	9.01718
% Cumulative expl. Var.	46.5156	63.8497	74.2135	83.2307

The third factor is loaded by the ratio C/N in opposition to NaExch and the second factorial plan (Figure 5.14) contains 56.9% of the information in the correlation matrix and it explains 11 of the 14 variables. The fourth factor is loaded by clay in opposition to NaExch and KExch, and the third factorial plan (Figure 5.15) contains 55.5% of the information in the correlation matrix and it explains 12 of the 14 variables.

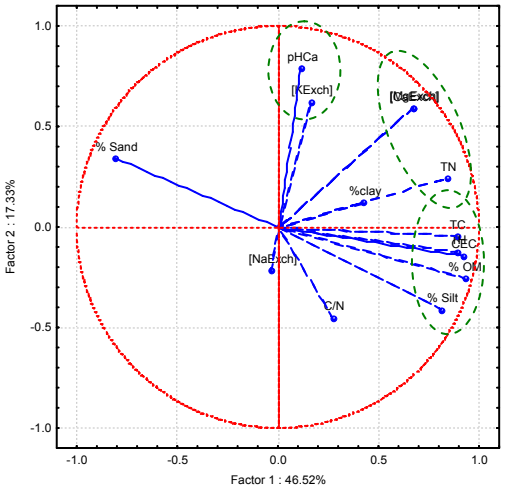


Figure 5.13 - Plot of the first factorial plan from PCA.

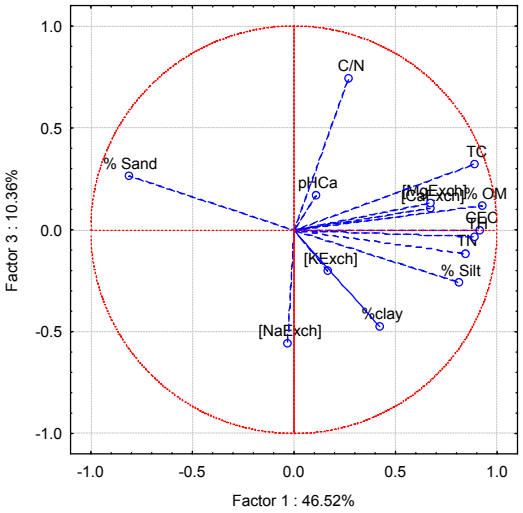


Figure 5.14 - Plot of the second factorial plan from PCA.

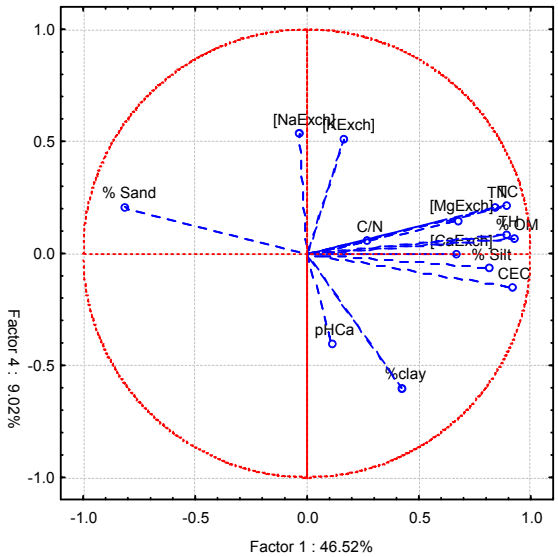


Figure 5.15 - Plot of the third factorial plan from PCA.

Therefore the application of PCAs allowed the observation of two groups of variables related to the first factor, being the first one constituted by silt, OM, CEC, total C and H,

whereas other soil properties such as TN, CaExch and MgExch seem to be associated among them and separated from the first group by the second factor. As it was expected sand showed a negative correlation with all this parameters. On the other hand, the pH showed an anomalous behaviour, has it is widely know to be dependent on the OM and CEC content. However, pH showed significant positive correlations with CaExch, MgExch and KExch, explaining the position of the first two parameters in the plot of the first factor plane (Figure 5.13). Moreover, the %BS is crudely correlated with soil pH (Pearson correlation of 0.661, $p<0.05$), what is expected for mildly acid and neutral soils (Ellis & Mellor, 1995). In what concerns to total N, it is known that it increases with pH (Russel, 1973), however any significant correlation was found. Nevertheless the highest values were found in samples 25.AG.SF and 23.AG.SB, which have a high pH value.

Distribution of factor-scores, indicating the relative strength of the first factor (explained variance of 46.52%) in each sample is given in Figure 5.16. The positive anomalies on the first factor score map (Figure 5.16) indicate the high contribution of OM, CEC, TCNH, silt, CaExch and MgExch. Samples in which these parameters are having a highest contribution are sample 6.RD, 14.PO and 25.AG. The negative anomalies represent samples that have a high contribution of sand and they seem to have a similar distribution over the study area. On the other hand the positive anomalies are located mainly in the city centre. Distribution of factor scores of the second factor is not shown as the distribution was found to be similar over the study area, indicating that the high content in MgExch, CaExch and KExch is a characteristic of most Estarreja soils.

These results, together with the scatter of all sampling points plotted on the first factorial plane (Figure 5.17), turn it possible to extract some conclusions about characteristics of each sample. It can be highlighted the position of sample 11.RD, which has very specific characteristics, being classified as sandy, with a neutral pH and very low content of OM, TCNH, CEC and exchangeable cations. Sample 14.PO and 25.AG are plotted in opposite sides, and also isolated from the others. This fact is due to differences in the texture, as sample 14.PO is classified as silt loam and sample 25.AG as sandy loam (however, very close to be classified as loam, Figure 5.11). Both samples have very high contents of OM, TCNH and CEC however sample 25 is neutral with higher content of exchangeable cations and probably soluble salts (Table 5.6) and on the other hand sample 14 is acidic, with lower content on exchangeable cations. These differences explain that they are separated by the second factor, responsible for the pH and KExch.

Sample 26.AG and 9.OG/RD, are plotted in opposite sides (Figure 5.17), mainly due to the neutral pH and highest value of KExch (and other cations) in sample 26.AG and the acidity and low KExch (bellow detection limit) for sample 9.OG/RD. These samples are separated by the first factor and, as OM and CEC are low for both, the major difference is TN and in the content of exchangeable cations, being the value of TN for sample 26 one of the highest found (Table 5.4 and Figure 5.6). In what concerns the exchangeable cations, sample 9.OG/RD has very low concentration of Ca and Mg, but the highest value of Na (Figure 5.8 and Table 5.6). Samples 22.AG and 18.AG, that shows low values of exchangeable cations and low pH, form a cluster with sample 9.RD.

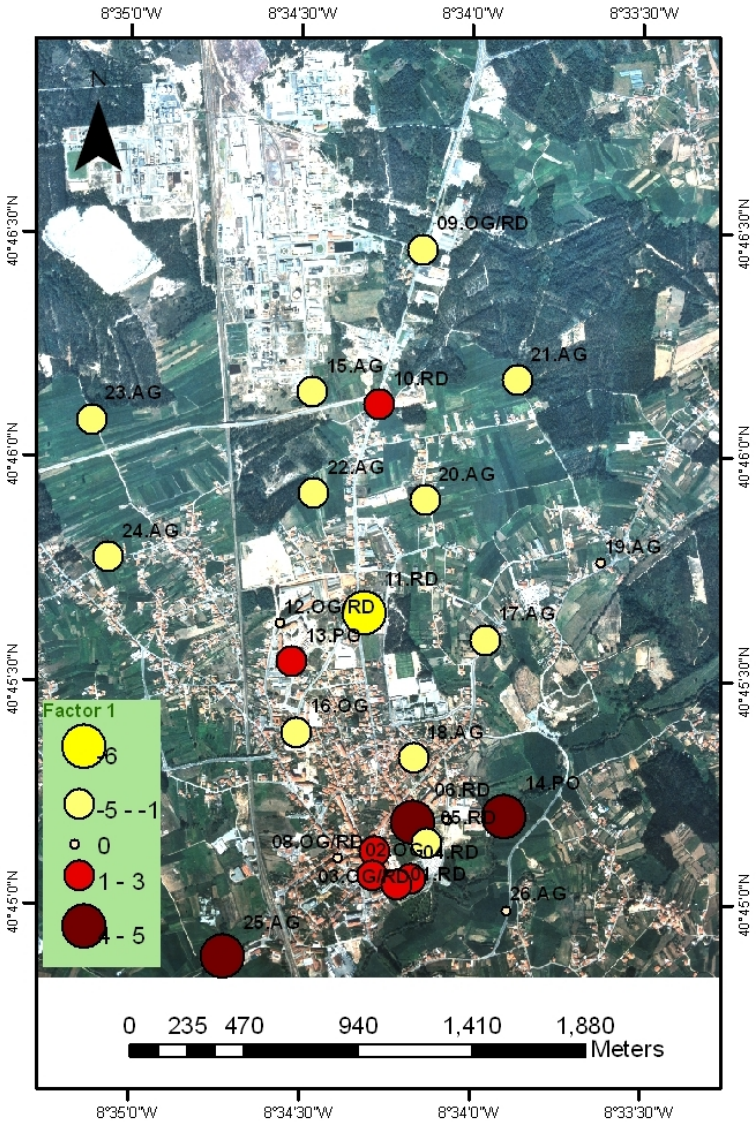


Figure 5.16 – Plot of factor scores for the first factor (OM, CEC, TCNH, silt, CaExch, MgExch in opposition to sand).

The ratio C/N is explained only by the third factor (10.36% of explained variance), in opposition to NaExch. The scatter of sampling points plotted on the second factorial plane is shown in Figure 5.18. Sample 26.AG, as for the first factorial plan is isolated from all others, being in this case due to the low value of C/N. Samples 9.OG/RD, 10.RD, 18.AG and 24.AG have a C/N ratio close to 10, but they have high percentages of Na, being classified as sodic samples. In Figure 5.18 it's possible to see that they form a cluster, however sample 10 is separated by the fist factor due to its highest content in OM. Another group can be easily identified, which is formed by samples 2.OG, 3.OG/RD, 4.RD and 6.RD. All these samples have C/N ratios equal or higher than 10 and OM content near or above the median. No correlation or association was found between the pH and C/N ratio, however the lowest value of C/N ratio was found in sample 23.AG.SB that has a pH value of 7.2, the same pattern was found for sample 26.AG.

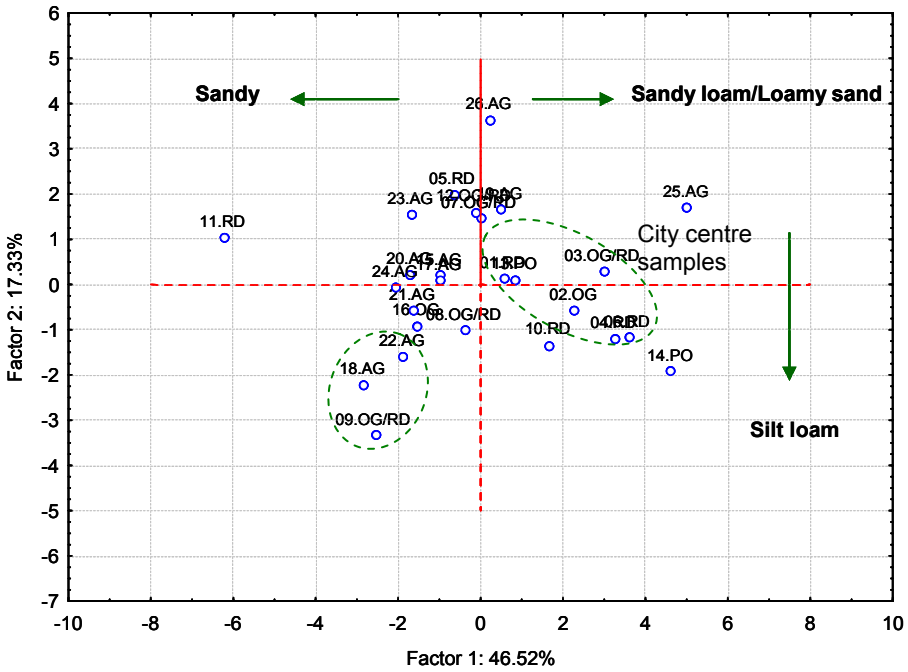


Figure 5.17 – Scatter of all sampling points plotted on the first factorial plane.

The fourth factor is the only one that explains the clay parameter but it also explains, in opposition to this one, the NaExch and KExch. Therefore it's easy to understand the position of sample 8.OG/RD in the scatter plot of the cases for the third factorial plan (Figure 5.19). This sample has the highest percentage in clay and very low NaExch and KExch, being this an OG it's probable that it is a foreign soil. However, similar

characteristics were found in samples 2.OG, 3.OG/RD, 6.RD and 21.AG. Another group can be identified (samples 20.AG, 7.OG/RD, 10.RD and 4.RD) by having low clay percentages and high content of NaExch or KExch.

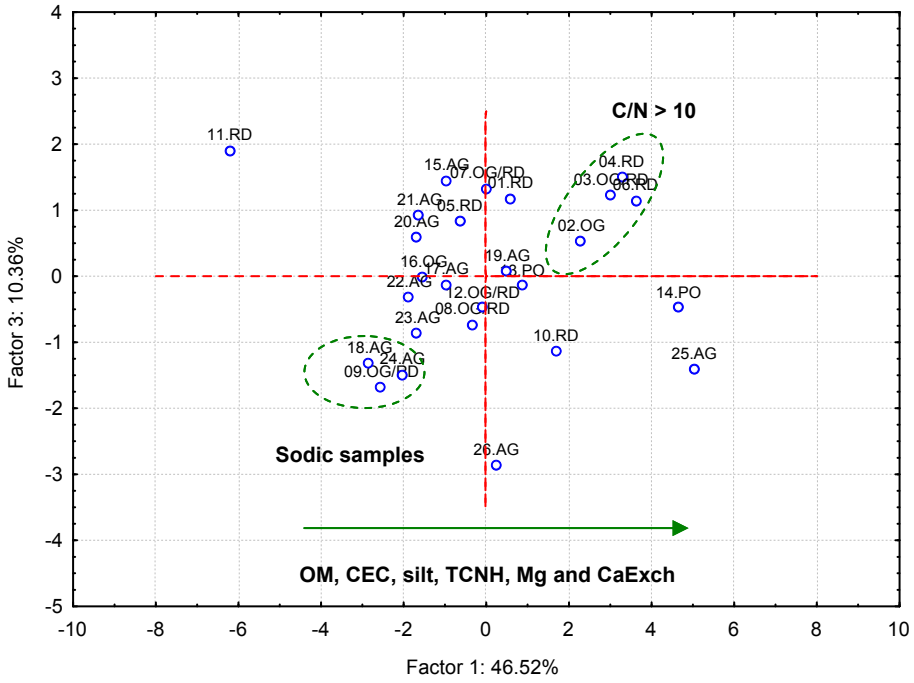


Figure 5.18 - Scatter of all sampling points plotted on the second factorial plane.

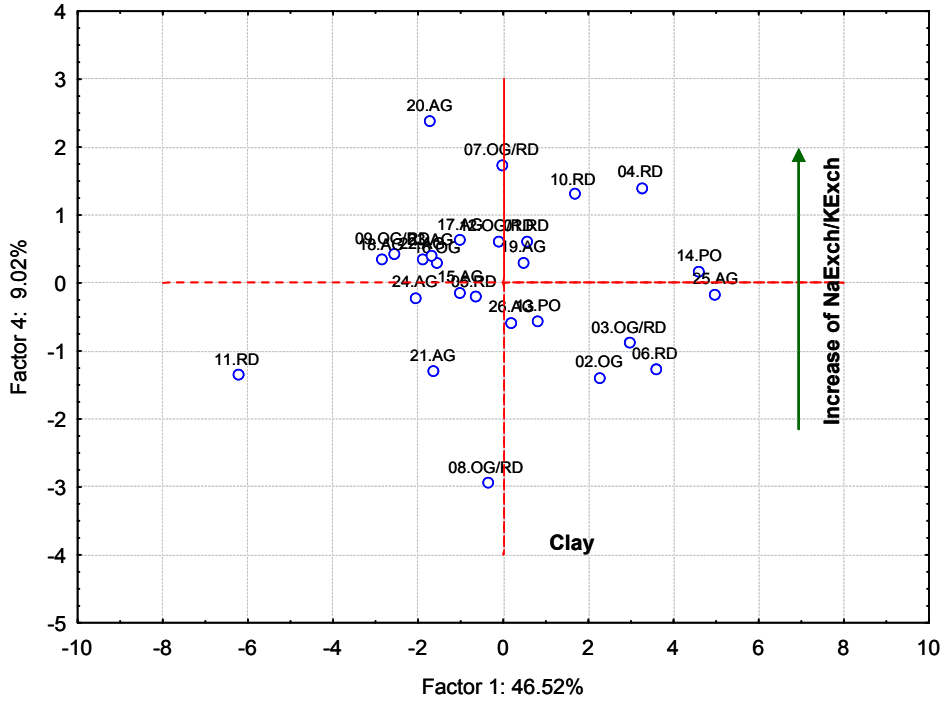


Figure 5.19 - Scatter of all sampling points plotted on the third factorial plane.

Physical characteristics of samples seem to be very important parameters which also influence other characteristics such as OM and CEC. Thus, heavy-textured soils (high contents of clay) have higher organic matter contents than loamy soils, which in turn have higher organic matter contents than sandy soils (Stevenson, 1982). In Estarreja most of soils sampled showed textures between loamy sand or sandy loam, resulting in a medium value of overall OM and CEC contents. Retention of substances may also be affected by the type of clay mineral present, although this was not studied.

One of the problems associated with sandy soils is that the shortage of fine particles limits the formation of a strong soil structure due to the lack of aggregating agents and bridging materials between coarse grains. The lack of organic matter will intensify this problem and soils fail to develop the granular or crumb structures normally developed in natural and agricultural topsoil (Jim, 1998), being example samples 11.RD, 18.AG and 22.AG. On the other hand, in soils with low clay content, an increase in SOM improves aggregation of soil particles, resulting in the development of stable soil structures (Huinink, 1998). It also increases the CEC, the water holding capacity, the soil's nutrient content, especially N and S, affecting the fertility (Tan, 1994). In this study two cases of the texture influence on other soil properties can be addressed. The first one is sample 14, classified as silt loam, shows the highest percentage of OM, low pH, high % of TN, TC, TH and high CEC and exchangeable acidity as it was expected according to the texture. The second one is sample 11 which results are according to the expected in what concerns the texture (sand): high pH, the lowest % of OM, TN, TC and TH, the lowest CEC and exchangeable acidity and a percent base saturation of 95.5 %.

Another important parameter affecting soils properties is soil pH. One of the main functions of soil is its buffering capacity of pH due to several properties (Wild, 1993): reactions of acids with calcium and magnesium carbonates; cation exchange; proton adsorption by clay minerals, humus, and hydrated aluminium and iron oxides; proton adsorption by aluminium ions; solubilization of soil minerals. As a result of soil's acidification their capacity to adsorb cations is reduced and nutrient cations, especially Ca and Mg, pass into solution and are leached in drainage water and the basic cations are replaced by protons and aluminium ions. If the basic cations losses are uptake by plants they can be returned to soil in litter or on the death of plants. C/N is an estimation of humus and humus is a source of exchangeable ions, therefore if there are no basic cations sufficient enough to balance the negative charge of humus the pH will decease (Wild, 1993). Another important implication of soil's pH is on the activity of micro-

organisms, that is responsible for breaking down organic matter and most chemical transformations in the soil, but the pH must be favourable for microbial activity which is not observed in most of Estarreja soils. In this way, pH is an important parameter to be measured in all quality assessment studies.

From the PCA results it can be defined a minimum data set of parameters to be determined in environmental quality assessments. In this case, and having in account the more important parameters affecting each factor, the following can be selected: pH, texture and TCNH. The parameters analysed are more or less related between them, being the texture probably the most important one affecting OM and CEC. The pH results can be an indication of base saturation, however in soils under marine influence Na can be at anomalous concentrations. From the Total C, N and H results, which are very simple to determine, it's possible to have an estimation of OM (for non carbonated soils) and C/N ratio. However, the relationship between OM and organic carbon is not equal in all soils, and therefore the estimation of OM by LOI, which is very simple and cheap, can be helpful and improve the data set of a quality assessment. Furthermore, the data set chosen should depend on the study aims. For example, texture that is an indicator of other soil properties, by itself it cannot be used to estimate the ability of soil to adsorb cations from solution, as it depends on the mineralogy of the clay fraction as well as on the amount and nature of OM (Wild, 1993).

5.3.4 Effects of land use on indicators selected

In order to detect differences between land uses Kruskal-Wallis One Way Analysis of Variance on Ranks test was performed. Table 5.8 shows the median values for each parameter by land use, the samples classified as OG/RD were now classified only as OG due to the management that they are submitted.

Parks and ornamental gardens were expected to have an accumulation of organic matter (Schraps & Baumgarten, 2000), however, analysis of variance showed that differences between land uses are not statistically different. Still, the median value of %OM in parks was found to be the highest (7.2%) while agricultural sites, together with OG showed the lowest median values of OM (Table 5.8). The agricultural samples also show a smaller difference between layers, as it's possible to see by the enrichment factor obtained for each sample (Table 5.5). It is usual to find low values of organic matter in agricultural soils with crop rotation and losses are known to be more or less linear with time, and ultimately it will reach an absolute minimum, approaching zero (Stevenson,

1982). Moreover, the C/N ratio, that is an indication of humus, showed statistically significant differences (One-Way ANOVA), in surface layers, between Agricultural sites and Roadsides. Soils carrying out natural vegetation, such as forest (sample 14.PO), typically have high humus content both because they have a higher rate of addition of OM and the soil is not disturbed. Moreover the level of OM in soils is determined by the rates of addition and oxidation of plant residues and of soil humus, topography, parent material and the age of soil (Stevenson, 1982).

Table 5.8 - General properties of the soil samples in surface layer (median values).

Parameter	Land use				
	AG	OG	PO	RD	Total
pH(H_2O)	6.2	6.2	6.0	6.2	6.1
pH($CaCl_2$)	5.0	5.3	5.2	5.2	5.2
TC (%)	1.7	2.2	2.9	2.8	2.1
TN (%)	0.2	0.2	0.3	0.2	0.2
TH (%)	0.6	0.9	1.2	1.1	0.8
OM (%)	4.1	4.2	7.2	6.1	4.4
C/N	8.2	10	11	11	9.5
CEC(cmolc/kg)	9.9	9.7	17	12	11
CaExch(cmolc/kg)	4.3	5.2	5.8	5.6	4.8
MgExch(cmolc/kg)	2.9	5.6	5.0	4.9	4.2
NaExch(cmolc/kg)	0.6	0.5	0.7	0.7	0.5
KExch(cmolc/kg)	0.2	0.3	0.1	0.1	0.2
Sand (%)	74	65	53	68	71
Silt (%)	21	30	41	28	25
Clay (%)	4.3	4.3	6.0	3.9	4.3

The median values of CEC seem to be different among land uses (Table 5.8), however no statistical difference between them were observed. The lowest median values of CaExch and MgExch were found in agricultural sites, what may be due to the removal of nutrients in harvested crops. The highest value of KExch and total N was found in an agricultural site (samples 26.AG and 25.AG), that may be an indication of sewage sludge application. It is also known that in agricultural soils the amount of cations applied in

fertilisers, lime or manures to land may have some influence on the composition of exchangeable cations (Russel, 1973).

Regarding the pH values it is known that the management of soils may alter the natural pH because of acid-forming nitrogen fertilizers, or removal of bases like potassium, calcium and magnesium. However no differences were found between land uses, the lowest pH value was found an agricultural site, but also the highest one, being the low pH values a characteristic of all Estarreja soils.

Effects of land use in texture and the geology of area couldn't be statistically proved. As in other cases, median values show some differences between the land uses, being the highest one for agricultural soils and the lowest one for parks.

In addition to this analysis, the scatter plot of sampling points on factorial plane, together with factor-scores map, can be an easy way to observe samples characteristics and conclude whether they are suitable for purpose or they should be subjected on any kind of management to improve their quality. For example, the low content of clay mineral allied to low C/N ratios will diminish soil physical conditions for plant growth.

5.4. Conclusions

Estarreja urban soils can be characterized as slightly acid, with medium to high contents in organic matter and total carbon, being the surface layer enriched with OM. The CEC values are low, and the low nutrient status turn this soils very infertile. Some samples showed very high percentages of NaExch, probably reflecting rainwater influence. Concerning the texture, Estarreja urban soils can be classified as sandy loam or loamy sand. Therefore, a high percentage of sand seems to be a natural feature of the studied area, however inner the city centre, which are mainly ornamental gardens, there is a slight difference, probably due to the introduction of foreign soils.

Physical characteristics of samples seem to be an important factor that influences other soil parameters. The presence of samples with very different texture classes, sandy and silt loam can reflect the impact of this parameter in OM and CEC content. Moreover, general parameters characterized were in accordance with the expected results due to soil type and management practices.

The pH is also an indicator that can influence other soil parameters, even that in this study this relationship was not so evident, probably because there is a low variability of pH in the set of sampling sites. The pH is especially important in what concerns nutrients availability and the solubility of potentially toxic metals. Soils from Estarreja are also

known to have high permeability, representing a threat for aquifers or surface streams, as soils cannot perform their role as sink of pollutants.

From the PCA results a minimum data set of parameters for environmental quality assessments can be selected: the pH, texture and Total C and N. Moreover, soil texture is an important property from which many other soil parameters can be estimated or inferred. However, used alone it can have limited predictive values, depending on the purpose. In addition, CEC is also important because of nutrients availability and indication of the buffer capacity of soil.

6. Distribution of potentially toxic metals in Estarreja urban area

6.1. Introduction

Trace elements are introduced into soil from both natural and anthropogenic sources. Major and trace elements in parent rocks may be included in the formed soil fractions or by atmospheric deposition of particles emitted from natural sources such as forest fires, volcanic activity and biogenic emissions (Alloway, 1995; Guvenç *et al.*, 2003). However, anthropogenic activities disturb the natural distribution of elements in soils.

Agriculture is one of the most important sources of metals in soils (especially Pb, Cd, Zn and Hg), by application of pesticides, fertilizers, sewage sludge or due to irrigation water taken from polluted streams (Wild, 1993; Alloway, 1995). Potentially toxic metals (PTM), mainly Hg, Cu, Zn and Cd, are also commonly found in soils of areas where ore extraction and smelting occurred (Alloway, 1995). Domestic waste disposal, motorways and urban areas are other important sources of PTM in the environment (Koeleman *et al.*, 1999; Bityuoka *et al.*, 2000, Norra & Stüben, 2003), being in the last case the deposition of atmospheric particles over the years of major importance. There are also many studies showing the enrichment of heavy metals in soils around industrial sites (Bityukova *et al.*, 2000; Peltola & Åström, 2003). For example, steel industry is the main source of Cr and Ni, the manufacture of batteries of Cd and Pb and zinc plating factories of Zn. Emissions from chlor-alkali industry were during decades one of the major sources of Hg into the environment, however the development of new technology resulted in a decrease of emissions. Other important uses of metals include (Wild, 1993; Tan, 1994): pigment paints (Pb, Zn, Cd, Hg), for covering electrical cables (Pb), manufacture of plastics, glasses and glazes (Pb, Cd), as a filter in rubber and tyres (Zn), metal coating and alloys (Zn, Cd) and batteries (Zn, Cd). Hg has also been widely used for making thermometers, vapour and fluorescence lamps (Tan, 1994).

PTM may exist in soil in a number of forms including as adsorbed cations, attached to clay aluminosilicates and humus colloids, oxides of Fe, Mn and Al and organo-metallic chelates (Wild, 1993). Mobility of elements in soil is largely controlled by their solubility in water (Barradas *et. al*., 1992). Furthermore, bioavailability to plants depends on a number of soil characteristics, particularly cation exchange capacity (CEC), pH, organic matter content (OM), speciation of elements and the interdependence effects of other metals (Vangrosveld *et al.*, 1996). Moreover they enter the food chain either through water supplies and aquatic organisms, or through agriculture products and grazing animals. In addition, PTM have long residence time in soils. The effects of PTM in soils on human health are unclear, and it's therefore difficult to establish threshold concentrations above

which toxic problems are likely to occur. For example, Cd it is known to cause renal and testicular damage and Pb is implicated in causing liver damage (Tan, 1994). Mercury is one of the most important pollutants, due to its toxicity to man and many higher animals and the predisposition to accumulate in different environments (bioconcentration potential) (Lindberg, 1998; Manta *et al.*, 2002). Nerveless, some metals such as Cu, Mn and Zn are micronutrients which are essential in small amounts for plant and animal life, but due to human activities or natural causes they can be present in anomalous concentrations and may become toxic (Ellis & Mellor, 1995).

This chapter aims to assess the quality of urban soils from Estarreja, by using PTM as indicators, and therefore discriminate natural and anthropic contributions as well as point and non-point sources of contamination. The pseudo-total content of PTM was chosen as indicator because it provides more useful information than a total analysis as residual components are usually less available and therefore pose a little threat to the environment. At the end it will be identified the main factors controlling metals distribution in soils (natural causes, industry, traffic).

6.2. Methodology

Concentrations of eight potentially toxic metals (Zn, Cd, Ni, Cu, Pb, Cr, Fe and Mn) were determined using Atomic Absorption Spectrometry (Model GBC series 906 AA) after digestion with Aqua Regia. One gram of sample (weighed to the nearest 0.001 g) was digested with Aqua Regia (3 ml hydrochloric acid, 37% + 1 ml nitric acid, 65%) in a Teflon baker. The mixture was gently heated on a hotplate at 100°C until dryness. After this, 10 ml of HNO_3 4N were added to the Teflon vessels and the solution was transferred to a 25 ml volumetric flask and made up to volume with demineralised water. Solutions were centrifuged (5min at 4000 rpm) and filtrated by means of MN 640 filter papers to 50 ml PVC flasks. When it was necessary, dilutions were made by adding 9 ml of HNO_3 4N to 1 ml of solution.

The determination of total Hg concentrations was performed by pyrolysis atomic absorption spectrometry with gold amalgamation (LECO model AMA-254), being the analyses performed directly on soil samples.

Determinations of all metals were undertaken in the <150 μm fraction for both surfaces in a total of 50 samples.

6.2.1 Quality control

For the determination of potentially toxic metals, the instrument was calibrated with five acidified standards and a standard was analyzed every ten samples to check for instrument drift. The calibration series used ranged from 0.25 to 5 mg/l for Cu, Zn, Cr, Pb, Mn and Ni, from 2.5 to 50 mg/l for Fe and from 0.1 to 0.5 mg/l for Cd. The calibration solutions were prepared in the same extraction solution as the samples in order to remove the matrix effect. Detection limits were estimated from the calibration curve as the concentration giving a blank signal, plus three standard deviations of the blank. Table 6.1 shows the limits of detection (LOD) and percent recoveries of certified reference material for each metal analysed.

For quality assurance 3 replicate blanks were analysed and results were bellow detection limit for all parameters. Precision was evaluated by calculating variation between duplicate analyses, therefore 10% of samples were digested and analysed in duplicate being the relative standard deviation (RSD) bellow 10% for all replicates. All mercury determinations were made in duplicate and RSD was also bellow 10 % for all replicates.

Two reference materials were used: BCR 141R, calcareous loam soil and BCR 142R, light sandy soil. Reference materials were subject to Aqua Regia digestion, except for mercury, following the same procedure of samples.

Table 6.1 – Limits of detection (LOD) and recovery (%) for the nine PTM analysed.

	LOD	CRM 141		CRM142	
		Recovery (%)	STD (%)	Recovery (%)	STD (%)
Zn	0.10 mg/l	102	3	93	5
Pb	0.14 mg/l	104	3	107	7
Cd	0.01 mg/l	93	1	-	-
Ni	0.10 mg/l	93	5	91	1
Cu	0.11 mg/l	92	1	95	0.5
Mn	0.22 mg/l	88	2	84	3
Cr	0.16 mg/l	-	-	81	5
Hg	0.01 ng	96	2	96	3
Fe	1.96 mg/l	-	-	-	-

6.3. Results and Discussion

6.3.1 Concentrations of potentially toxic metals in Estarreja urban soils

Results of PTM concentration in each sample, together with histograms and results of the normality test Kolmogorov-Smirnov are shown in Annex IV. By performing the normality

test it was possible to conclude that Pb, Ni, Cd, Mn, Cr (in SB layer) and Fe (in the SB layer) have a normal distribution, and when looking to values of mean, median and skewness (Table 6.2), they seem to be uniformly distributed over the study area. On the other hand, Cu, Zn, Hg, Cr (in SF layer) and Fe (in the SF layer) do not have a normal distribution. This, together with other properties like high standard deviations, positive skewness and median values much lower than the mean, are characteristics that can be qualitative indicators of an anthropogenic origin of these elements (Guvenç *et al.*, 2003). Mercury is the most evident case suggesting anthropogenic sources, with the highest coefficient of variation and with three extreme values, being this element one of the most important problems of the studied area. Zn and Cu also show differences over 15 times between minimum and maximum concentrations and values extend far beyond the median. By observing Figure 6.1, which shows the box plots obtained for each element in both layers, it's possible to observe the differences between elements concentration, the dispersion of results (with the outlier values and extreme values) and differences between layers.

Median values were found to be similar for surface (SF) and subsurface layers (SB) for all metals, but slightly higher values were found in the SF layer for Zn, Cr and Mn. A t-test, for Mn, Pb, or Mann-Whitney Rank Sum Test, for Fe, Cd, Cr, Ni, Zn, Cu and Hg, was performed and in all cases it was not found any statistically significant difference between the two layers. Differences between layers for each individual sampling site can be observed in Figure 6.2, Figure 6.3 and Figure 6.4.

Zn showed a median value of 59.3 mg/kg for SF layer and 47.6 mg/kg for SB layer. The minimum value was found in sample 11.RD.SB (15.41 mg/kg) and the maximum value was found in sample 14.PO.SF (284 mg/kg in SB). Moreover, samples 11.RD and 14.PO were the samples showing, respectively, the lowest and the highest concentration of all metals.

In what concerns Cd, most of results were bellow detection limit being quantified only 15 samples. The median values were 0.61 and 0.51 mg/kg for SF and SB layers, respectively, being the minimum concentration 0.20 mg/kg, found in sample 15.AG.SF and the maximum 1.73 mg/kg, found in sample 10.RD.SF. Cu showed a median concentration of 28.4 mg/kg in the SF layer and a very similar value in SB layer (26.0 mg/kg), with a minimum of 8.9 mg/kg in sample 5.RD.SF and a maximum of 111 mg/kg in sample 10.RD.SF.

Table 6.2 - Descriptive statistics of Estarreja soil samples (values in mg/kg, except for iron).

Elements	n	Mean	SD	Min.	Max.	Median	1st Quartile	3rd Quartile	CoefVar	Skewness
CuSF	26	42.9	32.2	8.94	111	28.4	17.6	69.7	75.2	0.91
CuSB	24	33.5	24.6	9.58	107	26.0	16.4	41.0	74.0	1.76
NiSF	26	10.0	4.71	2.14	23.1	8.46	7.17	13.7	47.1	0.93
NiSB	24	8.62	4.25	2.14	16.7	8.14	5.57	10.0	49.2	0.60
ZnSF	26	88.7	70.3	20.6	284	59.3	35.4	123	79.3	1.53
ZnSB	24	64.8	44.4	15.4	164	47.6	34.4	98.7	68.5	1.18
CdSF	15	0.80	0.49	0.20	1.73	0.61	0.41	1.27	61.6	0.45
CdSB	15	0.63	0.38	0.25	1.43	0.51	0.31	0.97	60.8	0.92
PbSF	26	35.7	15.7	12.3	65.8	34.7	23.2	45.8	43.8	0.58
PbSB	24	35.1	15.2	13.2	78.1	33.8	23.0	41.0	43.2	1.19
CrSF	26	17.2	11.1	5.32	54.5	14.6	7.98	22.9	64.3	1.57
CrSB	24	14.8	8.93	5.32	45.2	12.6	8.15	21.3	60.5	1.79
HgSF	26	0.48	0.94	0.05	4.53	0.20	0.12	0.32	196	3.67
HgSB	24	0.40	0.71	0.05	2.99	0.18	0.01	0.25	176	3.09
MnSF	26	152	71.2	29.3	295	146	91.9	212	46.9	0.37
MnSB	24	141	73.1	24.6	284	125	71.0	204	52.0	0.18
FeSF (%)	26	1.20	0.70	0.40	2.88	1.02	0.66	1.71	58.2	1.10
FeSB (%)	24	1.05	0.50	0.45	1.96	1.02	0.60	1.30	47.2	0.65

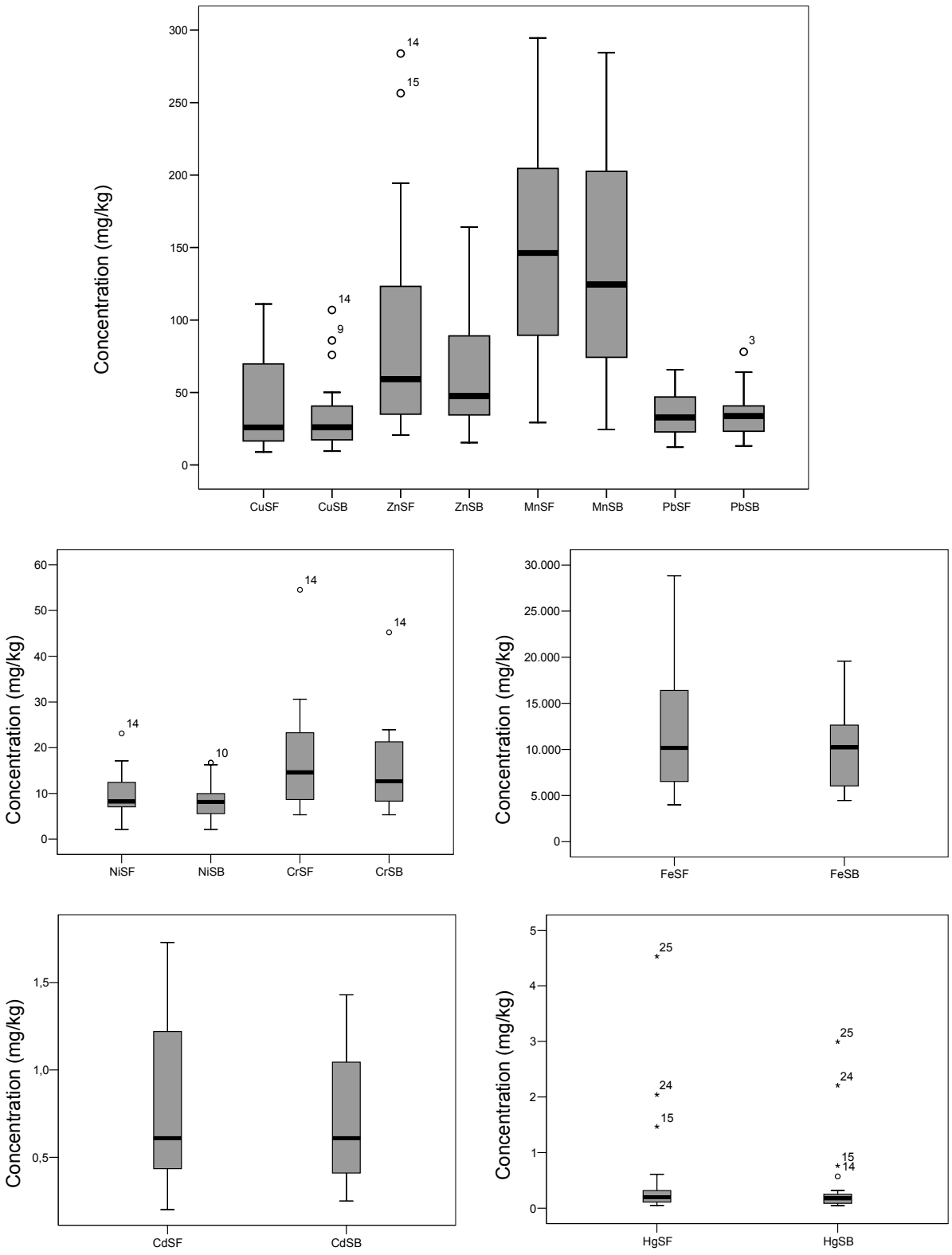


Figure 6.1 - Box-plots showing the variation of metal concentrations in both layers. Boxes define the interquartile range and the line is the median. Outliers (values between 1.5 - 3 box lengths) and extreme values (more than 3 box lengths) are also shown.

Hence, it's possible to conclude in a first instance that concentrations of PTM in Estarreja urban soils are low, with some sites showing higher concentrations probably due to point source contamination.

Barradas (1992) studied the geochemistry of the area near the chemical complex and found median concentrations (total content) of 18 mg/kg for Cu, 106 mg/kg for Zn, 53 mg/kg for Pb, 21 mg/kg for Ni, 19 mg/kg for Cr and 2.0 mg/kg for Cd. Batista *et al.*, (2002) found similar median total concentrations around the industrial area (16 mg/kg of Cu, 48 mg/kg of Pb, 84 mg/ kg of Zn, 21 mg/kg of Ni and 20 mg/kg of Cr). Barradas (1992) concluded that Pb, Zn and Cu have an anthropogenic origin, being the background estimated of 20 mg/kg for Cu, 60 mg/kg for Pb and 130 mg/kg for Zn. Figure 6.3 shows which samples are above the background estimated for these metals, being Cu the most problematic element, with many samples above this value, and for Zn and Pb only a few samples are above the background. In order to estimate the enrichment of the city with respect to the background estimated for these metals, a Pollution Index (PI=mean Estarreja/mean background) were calculated. Only Cu showed a value higher than one, being the ratio for this metal 2.14.

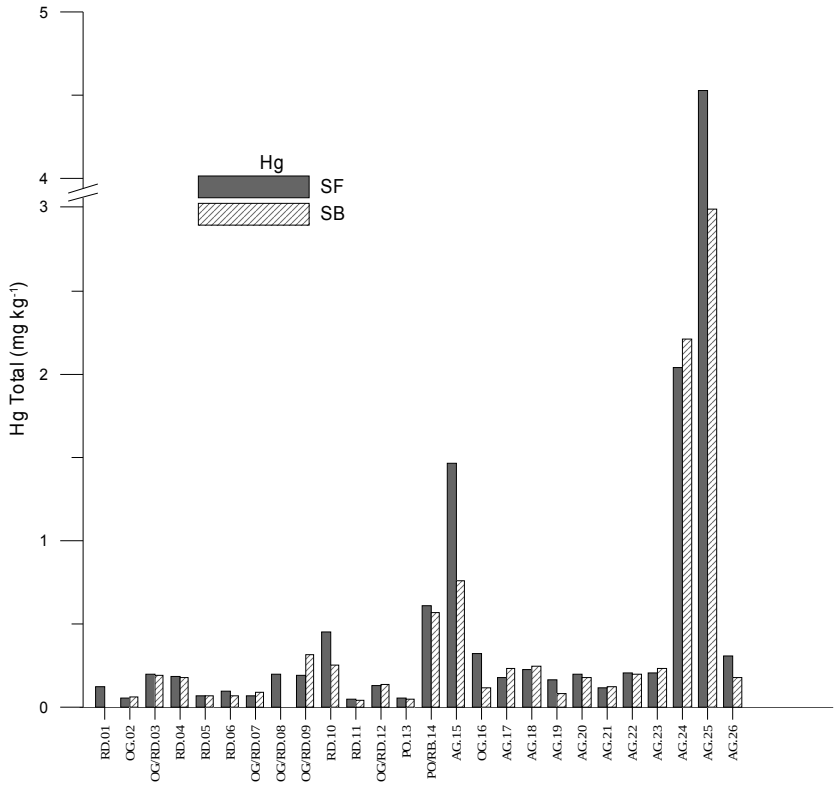


Figure 6.2 - Concentration of total Hg in each sampling point at two depths.

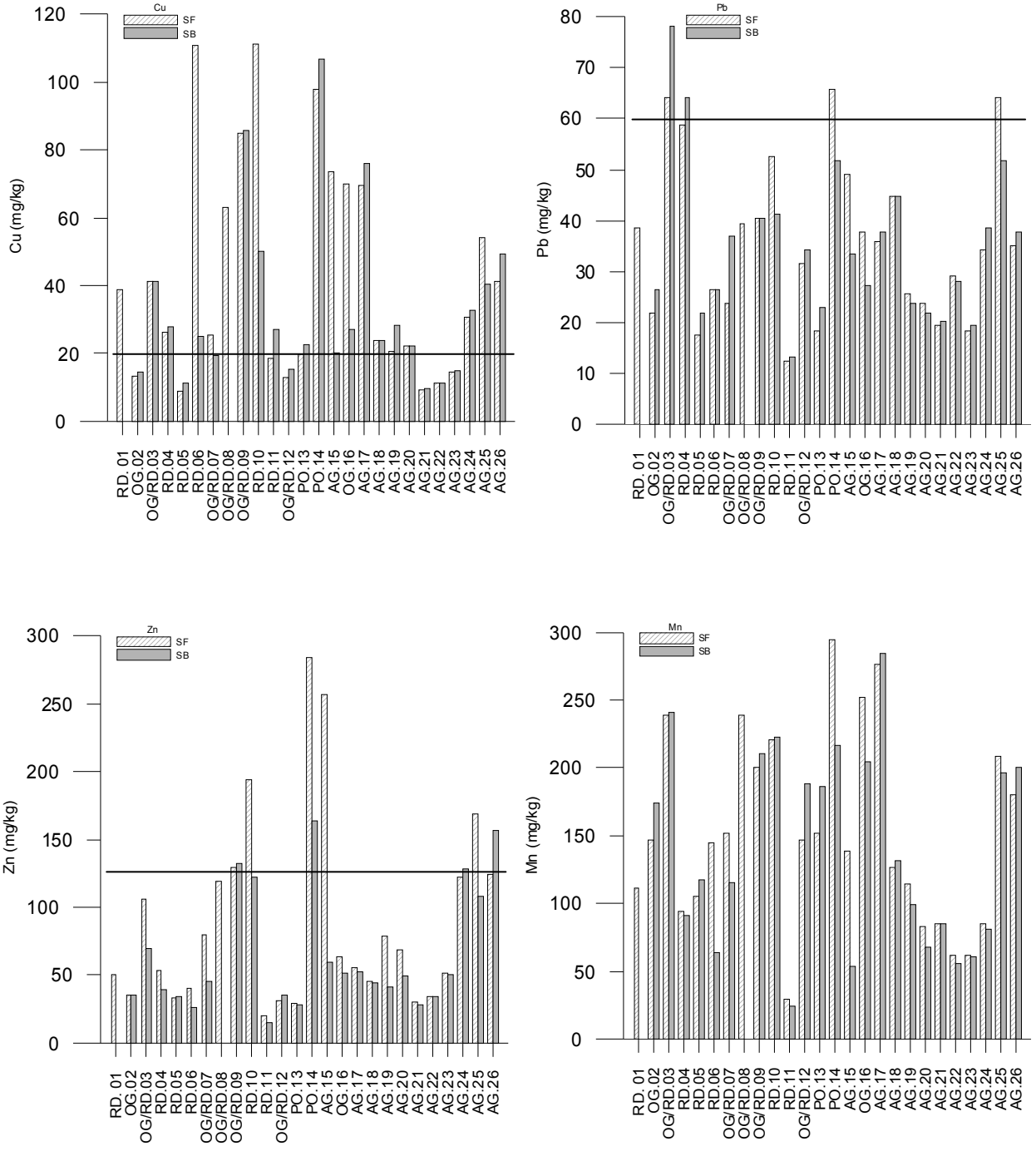


Figure 6.3 – Concentration of Cu, Pb, Zn and Mn in each sampling point at two depths, being the line the background values (Barradas, 1992).

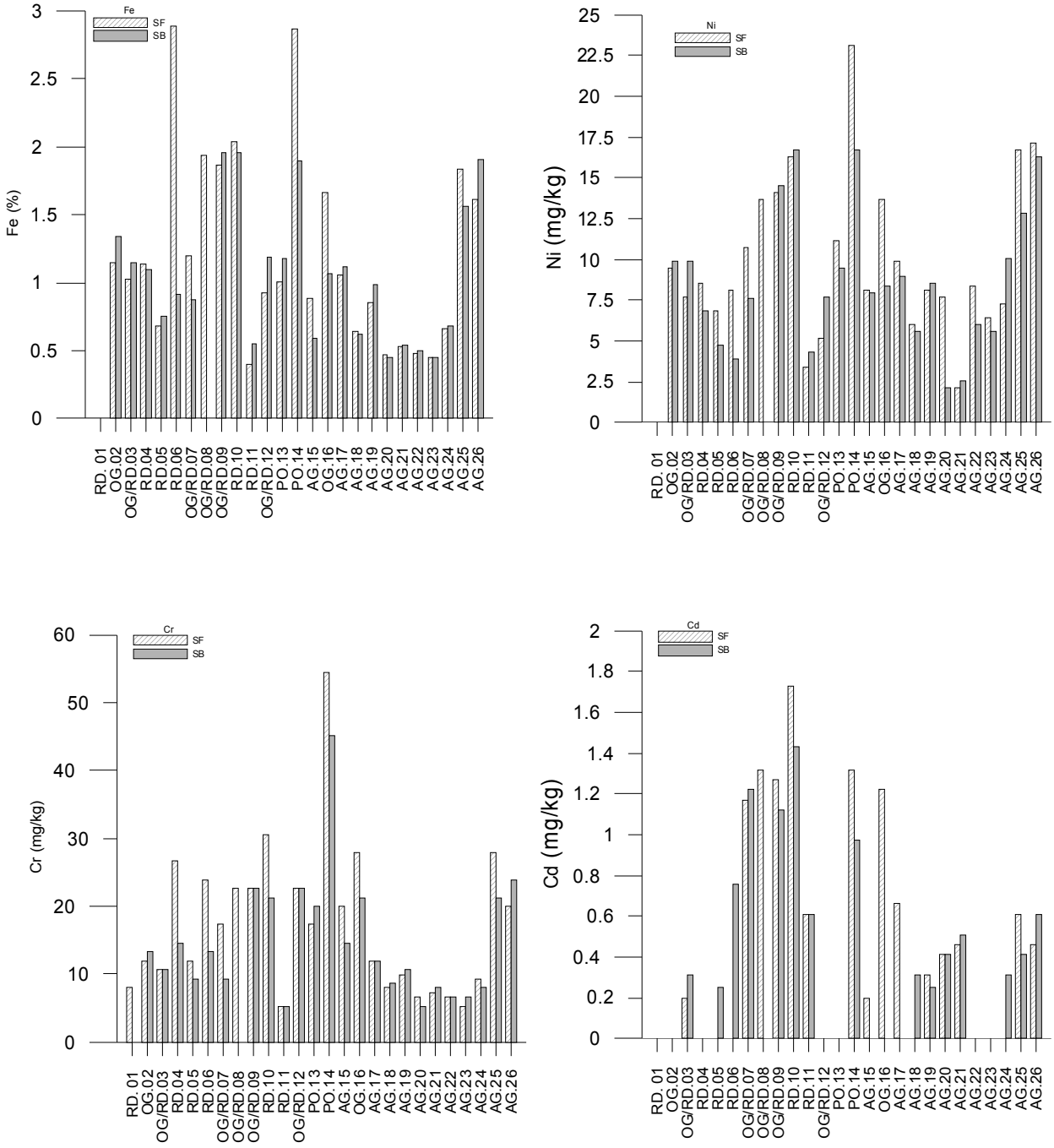


Figure 6.4 - Concentration of Fe, Ni, Cr and Cd in each sampling point at two depths.

In the particular case of total Hg, median concentration obtained for SF layer was 0.20 mg/kg and for SB layer 0.18 mg/kg ranging from 0.05 (samples 11.RD and 13.PO) to 4.53 mg/kg (sample 25.AG.SF). These values are lower than the ones found in previous studies of soils in the vicinity of the chemical complex (within an area of 10x6 km^2), where a median value of 0.59 mg/kg was found, ranging from 0.12 to 49 mg/kg. However, the highest values were found near the complex and lowest values (lower than 0.59 mg/kg) were observed in more distant areas, being comparable with the ones found in this study (Inácio *et al.*, 1998). On the other hand, concentrations of Hg in Estarreja are higher than concentrations found in Aveiro urban area, a bigger town (73 5000 inhabitants) 15 km away from Estarreja, were a median value of 0.09 mg/kg, ranging from 0.01 to 0.6, was found (Rodrigues *et al.*, 2006). Therefore, and considering the median concentration of Hg in Aveiro urban soils as background, the PI of Estarreja, in what concerns Hg, is 5.34.

In order to better understand the meaning of the results obtained they should be compared with the maximum acceptable limits established and with other case-studies. When comparing values obtained for Estarreja with other studies its possible to conclude that median concentrations of Zn, Pb and Cr are lower than values found in other cities like Wolverhampton (Kelly & Thornton, 1996), Tallin (Bityukova *et al.*, 2000) or than Palermo (Manta *et al.*, 2002) (Table 6.3). However these are bigger cities, for e.g. Wolverhampton, in UK, has 175,000 inhabitants and Estarreja has only 28,000 in the entire municipality. On the other hand, smaller cities like Jakobstad, an industrialized town with 20,000 inhabitants in west Finland where topsoil samples were found to be enriched in most elements (Peltola & Åström, 2003), showed concentrations comparable with Estarreja, which has some elements showing higher median concentrations (Table 6.3). Nevertheless, the range of results is in general much higher in other cities than for Estarreja showing the existence of few hotspots or point sources of pollution.

Mercury in Estarreja seems to be the most problematic pollutant, especially when compared with other cities. The average mercury concentration in soils over the world (Manta *et al.*, 2002) is reported to be from 50 to 100 µg/kg, and Estarreja showed a median concentration two times greater than the max mean value. Moreover, concentration of Hg in Estarreja is higher than in Berlin urban area (Birke & Rauch, 2000), Jacobstad (Peltola & Åström, 2003) or Antalya (Guvenç *et al.*, 2003). Higher concentrations are reported in soils from urban locations like Palermo (Manta *et al.*, 2002) and close to sources of Hg pollution (smelting, mining, coal burning facilities, chloralkali

industry, etc). For example, Bernaus *et al.* (2006) reported values as high as 1150 mg/kg in the surroundings of a chlor-alkali plant in the Netherlands.

Nevertheless, concentrations of PTM will be dependent of pedo-lithological conditions, being difficult to compare with other locals with different parent materials. For example, background levels of lead are reported to be less 100 mg/kg in uncontaminated soils (in Britain) (Ellis & Mellor, 1995), however the mean ranges from soils over the world are from 22 to 44 mg/kg (Manta *et al.*, 2002), and in France the reference values are 31 mg/kg. In the particular case of Estarreja, were the underlaying rocks are mainly sandy rocks, it is expected very low levels of trace elements as result of dissolution and chemical weathering (Bityokova *et al.*, 2000). Other problems when comparing studies may be differences in sample collection or determination methods (e.g. total vs. pseudo-total content).

Table 6.3 – Concentration of Cu, Zn, Pb, Cr, Ni, Cd, Mn and Hg in Estarreja urban soils, values from other cities and reference vales for comparison (median values unless when mentioned).

	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Hg (µg/kg)
Estarreja	28	59	35	15	9	0.6	146	200
Tallin, Estonia[1*]	35	114	50	33	15	-	320	-
Jakobstad[2*]	22	82	59	23	7.9	0.25	209	93
Berlin[3]	31.2	129	76.6	25.1	7.7	0.35	-	190
Wolverhampton, UK (mean values)[4]	62	231	106	-	-	0.8	-	-
Richmond, UK (mean values)[4]	30	108	158	-	-	<0.2	-	-
Antalya, Turkey[5*]	44	189	36.5	190	81.5	1.33	880	90
Palermo, Italy[6]	63	138	202					680
Reference values from France[7]	14	66	31	-	-	0.28	-	-
Soils over the world (mean ranges)[6]	13-24	45-100	22-44	12-83	12-34	0.37-0.78	270-525	50-100

[1]Bityukova *et al.*, 2000; [2]Peltola & Åström, 2003; [3]Birke & Rauch, 2000; [4]Kelly & Thornton, 1996; [5]Guvenç *et al.*, 2003; [6]Manta *et al.*, 2002; [7]Baize & Sterckeman, 2001. [*]Total content.

In Portugal there are only guidelines for agricultural soils, but for example guideline values for Québec and for Italy may be used, as they are both specific for residential and recreational soils. The Dutch guidelines define the Target Value (TV) as the baseline

concentration value below which compounds and/or elements are known or assumed not to affect the natural properties of the soil. Guidelines existing in several countries are shown in Table 6.4.

Table 6.4 – Quality guidelines or target values established in some countries for residential, recreational and agricultural areas (mg/kg).

	Canada[1]		Italy[2]	Portugal[3]	Netherlands[4]	Denmark[5]	Sweden[5]
	Residential	Agricultural	Residential	Agricultural	Target values	Target values	Residential
Cr	64	64	150	50/200/300	100	500	120
Pb	140	70	100	50/300/450	85	40	80
Ni	50	50	120	30/75/110	35	30	35
Zn	200	200	150	150/300/450	140	500	350
Cu	63	63	120	50/100/200	36	500	100
Cd	10	1.4	-	1/3/4	0.8	0.5	-
Hg	6.6	6.6	-	1/1.5/2	0.3	1	-

[1]Canadian environmental quality guidelines (CCME- [w_{14}]); [2]Biasioli *et al.,* 2006; [3]Portaria n.° 176/96. (pH <5.5/5.5-7/>7.0); [4] VROM, 2000; [5] Sanaterre -[w_{15}].

Considering the target values from Netherlands, it was found that 11 sites sampled were above this value for Cu (01.RD, 03.OG/RD, 06.RD, 08.OG/RD, 09.OG/RD, 10.RD, 14.PO, 15.AG, 16.OG, 17.AG and 25.AG), 4 sites for Zn (10.RD, 14.PO, 25.AG and 26.AG), 6 sites for Cd (7.OG/RD 8.OG/RD, 9.OG/RD, 10.OG/RD, 14PO, 16.OG) and 7 sites for Hg (10.RD, 14.PO, 15.AG, 16.OG, 24.AG and 25.AG). Regarding the land use, 6 samples from residential areas (6, 8, 9, 10, 14 and 16) and 2 samples from agricultural sites (15 and 17) are above the Canadian Guidelines for Cu and/or Zn. Samples 15, 24 and 25 show values of mercury above the Portuguese legislation for agricultural sites.

6.3.2 Application of multivariated analysis to PTM results

PCA was applied to soil data to obtain some factors that summarize geochemical information aiming to identify relationships between the studied variables. As differences between layers were not significant only SF were used in the PCA. Concentrations obtained from chemical analysis of the 9 elements were log transformed, as not all elements showed a normal distribution, and therefore the initial matrix was constituted by 26 individuals and 9 variables. In this way, the eigenvalues, extracted by PCA for log data, are presented in Figure 6.5. From the factorial axes obtained only the first 2 were

considered because they explain by themselves 77% of total variance and they have eigenvalues higher than unit. Table 6.5 shows the factor loadings (with the ones higher than 0.5 marked in bold) and percentage of explained variance of the factors considered. Projections of the variables in the first factorial plan, defined by axis 1 and 2, are shown in Figure 6.6.

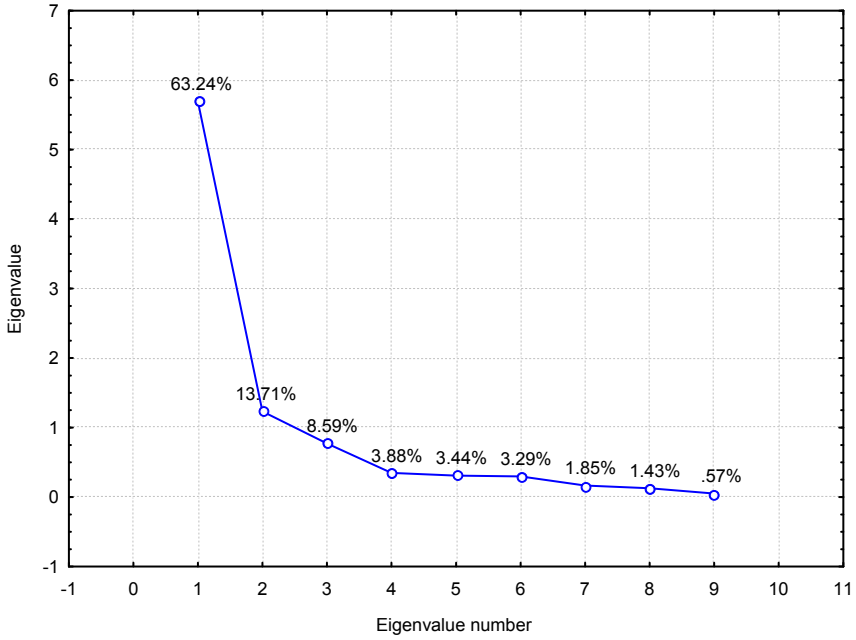


Figure 6.5 – Scree plot showing the 9 eigeinvalues obtained.

Table 6.5 – Factor loadings, eigenvalues and percent of variance.

Element	Factor 1	Factor 2
Cu	**-0.868977**	-0.029838
Pb	**-0.802411**	0.372577
Zn	**-0.843273**	0.386912
Mn	**-0.842570**	-0.254356
Fe %	**-0.874494**	-0.377413
Ni	**-0.841229**	-0.126049
Cr	**-0.849835**	-0.268054
Cd	**-0.581802**	-0.277120
Hg	**-0.581549**	**0.756805**
Eigenvalue	5.691339	1.233833
% Expl. variance	63.23710	13.70925
% Cumulative expl. var.	63.2371	76.9464

By observing Table 6.5 and Figure 6.6, where the projection of the first plan is represented, it's possible to conclude that the first factor (with an explained variance of 63.24%) has high loadings from all the variables by the following order: Fe, Cu, Cr, Zn, Mn, Ni, Pb, Cd and Hg. Hg is also explained by axis 2, being even more important. In Figure 6.6 it's possible to observe the association between the variables Cu, Cr, Ni, Cd, Mn and Fe. These are typical lithogenic elements (except Cu), probably associated to the local geology, therefore the natural sources are likely to be explained by the first factor.

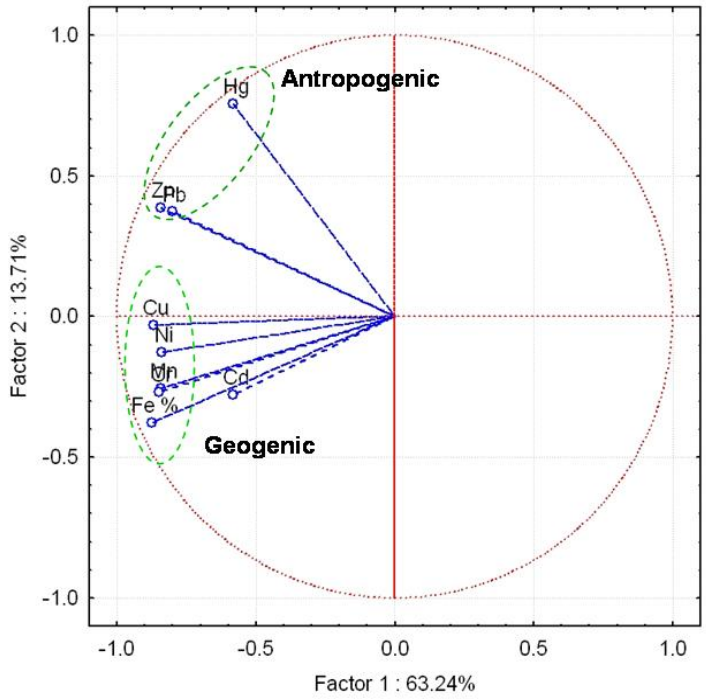


Figure 6.6 - Projection of the variables on the first factorial plan.

The second factor is responsible for 13.7% of the explained variance. It is loaded by Hg, but Zn and Pb appear to be associated with this element. Moreover Hg only showed significant correlations (Pearson correlation, $p<0.05$) with these two elements, meaning that the origin could be the same. It can be also observed the high correlation between Zn-Pb. In addition the association between Zn, Pb, Hg in this area as been reported in previous studies (Barradas, 1992; Batista *et al.*, 2002). Therefore, the second factor represents anthropogenic component in soil, as it is loaded by a typical anthropogenic element of Estarreja area.

Spatial distribution of factor-scores for the first and second factors is given in Figure 6.7 and Figure 6.8, indicating the relative strength of both factors in each sample. The

negative anomalies on the first factor score map indicate the high contribution of factor 1, and the positive anomalies on the second map indicate the contribution of factor 2 (anthropogenic sources).

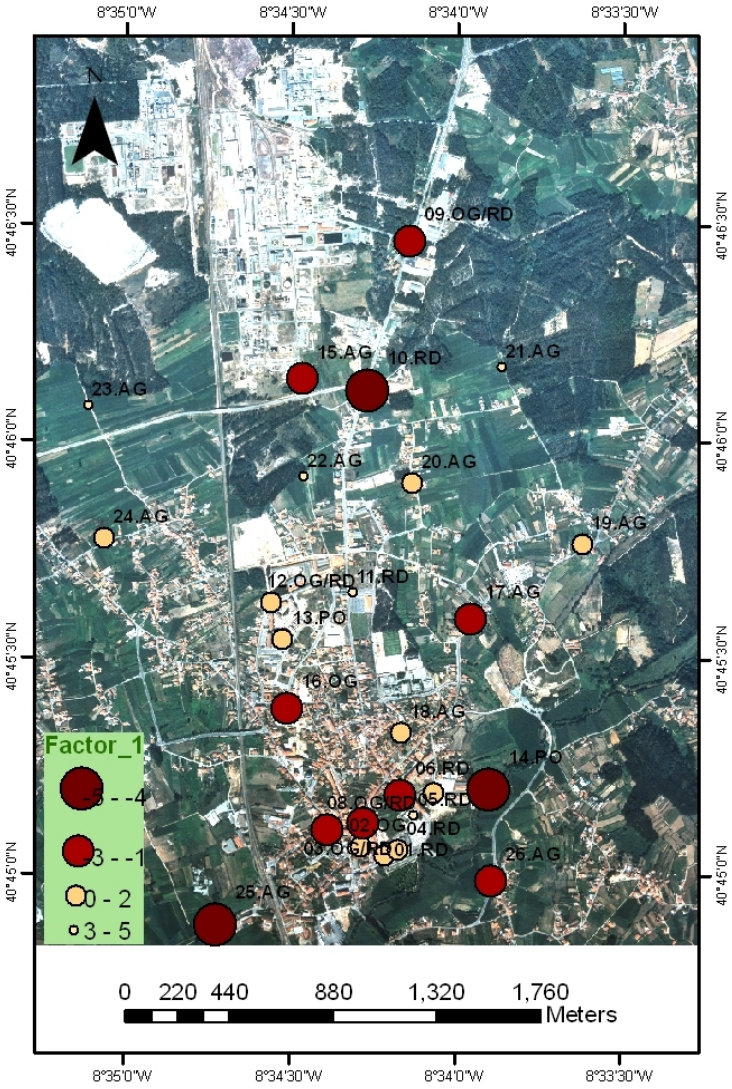


Figure 6.7 – Distribution of factor scores for the first factor for topsoils of Estarreja (Fe, Cu, Cr, Zn, Mn, Ni, Pb, Cd, Cr and Hg).

Although factor 1 seems to represent the local geology, factor scores do not show a homogeneous distribution over the study area as it was expected. It can be observed in Figure 6.7 two areas where negative anomalies are more evident: one near the chemical complex and other in the south of the study area, near the town centre. The main reason may be that this factor is loaded by elements such as Cu, Zn, Hg and Pb that are typical anthropogenic. On the other hand, factor 2, that conceptually condenses the information

of the Hg as tracer of anthropic pollution, shows strong positive anomalies in the area under the influence of the chemical complex (Figure 6.8). The predominance of northwest winds can result in a dispersion of atmospheric emissions from the complex to the south or southwest of the source. However a very strong anomaly was found in sample 25.AG that is located near the "Esteiro de Estarreja", which received contaminated effluents during decades. Moreover, Pereira *et al.* (1998) reported values from 49 to 340 mg/kg of Hg in surface sediments of the Esteiro, being the highest levels found nearby the effluent discharge point.

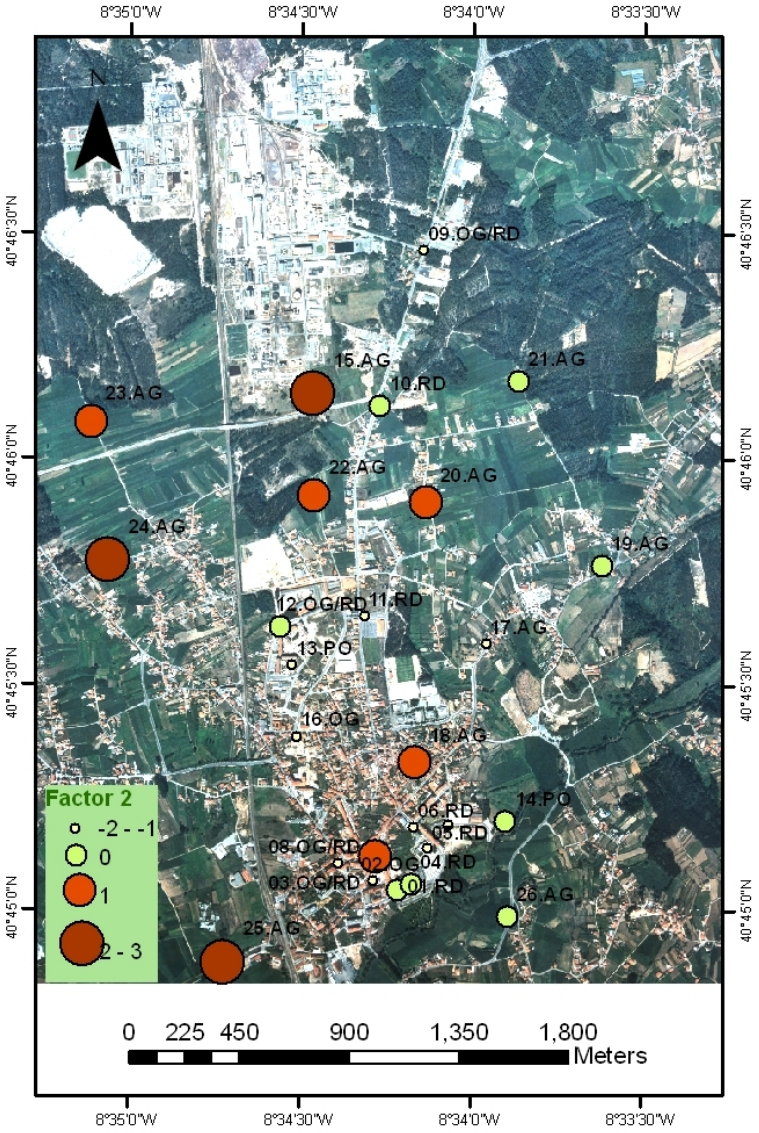


Figure 6.8 - Distribution of factor scores for the second factor for topsoils of Estarreja (Hg).

Figure 6.9, showing the projection of the cases on the first factor-plane, help on the visualization of factors contribution on samples distribution. Moreover it's possible to distinguish a group of 3 samples (15.AG, 24.AG and 25.AG) which are related to the association formed by Hg, Pb and Zn. Although sample 25.AG shows the highest Hg concentration, it does not have the highest positive anomaly when projecting the second factor score (Figure 6.8) due to high concentration of other metals, especially Pb and Zn. It is also possible to observe in Figure 6.9 the samples with higher (14. PO) and lower (11.RD) contents of most metals.

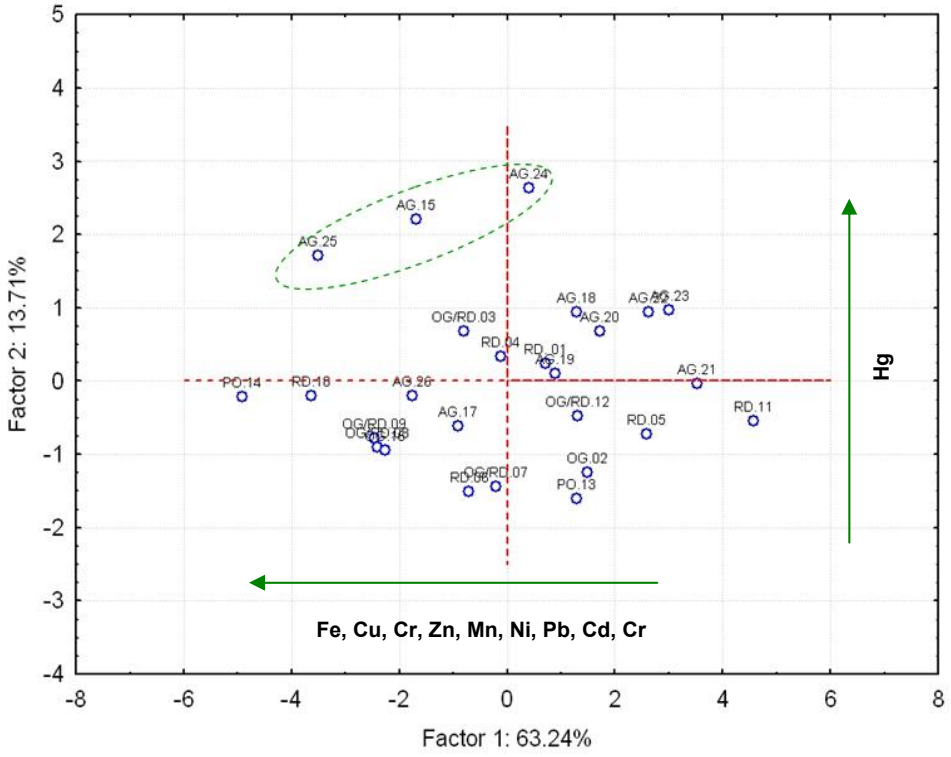


Figure 6.9 - Projection of the cases on the first factorial plan.

6.3.3 General soil parameters affecting PTM distribution

Some general parameters (OM, pH, TN, C/N, silt, clay and sand) determined in the previous chapter were included in the PCA analysis to identify their influence on potentially toxic metals (PTM) distribution. The 16 eigenvalues obtained, after log transformation, are shown in Figure 6.10. The first four axis shown in Table 6.6 have eigenvalues higher than unit, being the values in bold the factor loadings higher than 0.5, and they explain by themselves 80% of the total variance. Projections of the variables in the factorial plans are shown in Figure 6.11, Figure 6.12 and Figure 6.13.

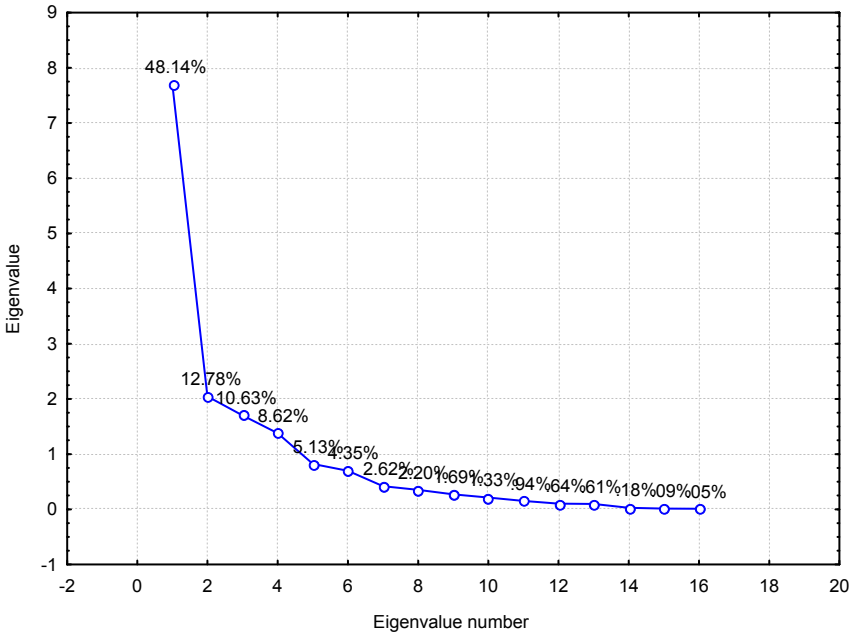


Figure 6.10 - Scree plot showing the 16 eigeinvalues obtained.

Table 6.6 – Factor loadings, eigenvalues and percent of variance.

	Factor 1	*Factor 2*	*Factor 3*	*Factor 4*
Cu	**-0.782976**	-0.389011	-0.209813	0.010877
Pb	**-0.803065**	-0.111440	0.080106	-0.409774
Zn	**-0.757202**	-0.442219	0.225623	-0.189719
Mn	**-0.839136**	-0.060673	-0.066060	0.197217
Fe	**-0.904772**	0.025096	-0.172971	0.321943
Ni	**-0.824863**	-0.187348	0.047215	0.081206
Cr	**-0.857427**	-0.010861	-0.163226	0.240703
Cd	-0.432133	**-0.649376**	-0.256865	0.307127
Hg	**-0.519836**	-0.356402	**0.527551**	-0.417095
pHCa	0.144678	0.155037	0.402452	**0.618709**
OM	**-0.742454**	**0.546051**	-0.102169	-0.235908
TN	**-0.518366**	**0.541732**	0.428463	-0.238485
C/N	-0.092412	0.389347	**-0.780755**	-0.153352
Sand	**0.857907**	-0.317935	0.041113	-0.093622
Silt	**-0.864005**	0.325435	-0.090320	-0.019105
clay	-0.378932	0.351390	0.465117	0.413840
Eigenvalue	7.70	2.05	1.70	1.38
% Total	48.14	12.78	10.63	8.62
Cumulative	48.14	60.92	71.55	80.17

By observing Table 6.6 and Figure 6.11, were the projection of the first factorial plan is represented it's possible to conclude that the first factor is loaded by the variables Fe followed by silt, Cr, Mn, Ni, Pb, Cu, Zn, OM, Hg and TN in opposition to sand. On other hand, the second factor its loaded by Cd in opposition to OM and TN. The factorial plan defined by the first two axes contains 60.9% of the total information of the correlation matrix, explaining 12 of the 14 variables.

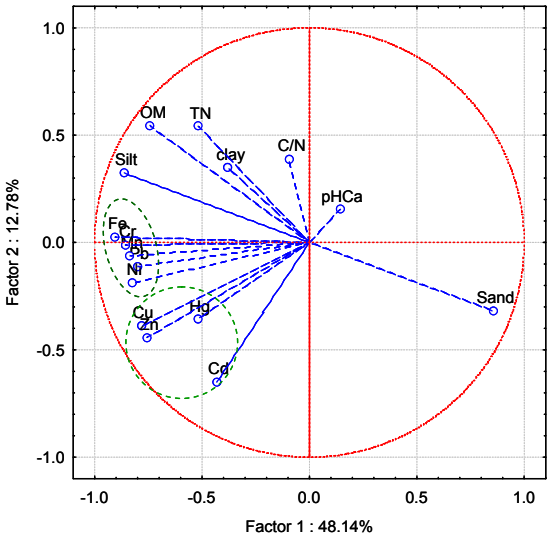


Figure 6.11 - Projection of the variables on the first factorial plane.

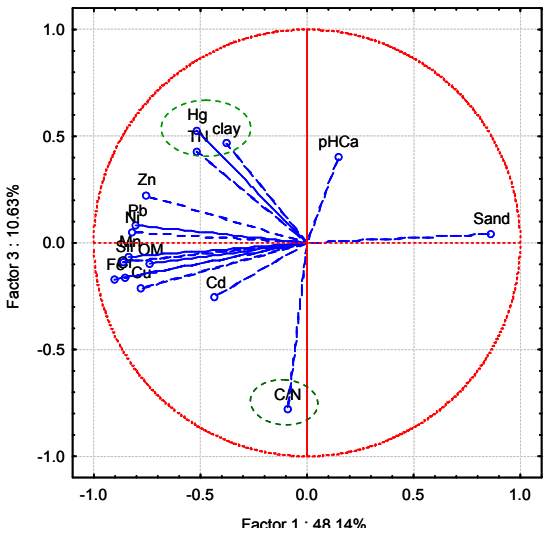


Figure 6.12 - Projection of the variables on the second factorial plane.

Analysing Figure 6.11 it's possible to observe the influence of texture and OM in the distribution of PTM, being evident two groups of elements which are suspected to have different sources. The first one is formed by Fe, Mn, Ni, Cr and Pb, being the first four associated with natural geology. The second group is formed by Cd, Hg, Zn and Cu which are elements likely to be affected by anthropogenic sources. Moreover, Zn, Cd and Hg do not show a positive correlation with OM. In addition, Cd and Hg, are not correlated with fine fraction. This behaviour may reflect the anthropogenic source of these elements as it is known that this factors control metal concentrations in soils (McMartin *et al.*, 2002).

The third factor is loaded by the C/N ratio in opposition to Hg. The second factorial plan (Figure 6.12) contains 58.8% of the information of the correlation matrix and it explains 12 of the 14 variables. In Figure 6.12 it's possible to identify the association between Hg, TN and clay (clay has only a factor loading of 0.46) and the influence of the C/N ratio on distribution of Hg concentrations.

The fourth factor is loaded by the pH_{Ca} and the third factorial plan contains 56.8% of the information. The pH is not having any important role in the PTM distribution as it was expected, however, from Figure 6.13 an association between OM, Zn, Pb, Hg and TN can be identified, separated from other group (Fe, Mn, Ni, Cr, Cu and silt) by the fourth factor. Even that it's not evident, this behaviour can be an indication of parameters that can be affected by pH.

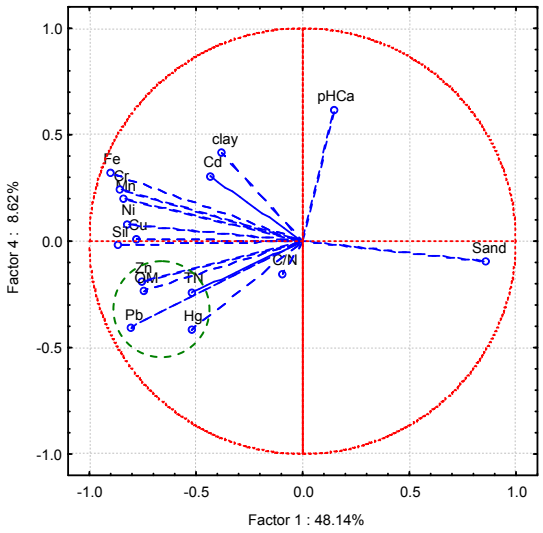


Figure 6.13 - Projection of the variables on third factorial plane.

Figure 6.14 gives the distribution of factor-scores for the first factor, where the negative anomalies are samples in which silt, OM and PTM are having a significant influence, whereas positive anomalies represents samples where sand is a more important factor. This distribution is very similar to the one showed in Figure 6.7 (distribution of factor scores for the first factor, when applying the PCAs to PTM levels). Therefore, it's possible to conclude that the distribution of PTM is influenced by samples characteristics such as OM and texture

Figure 6.15 gives the distribution of factor-scores for the second factor. The negative anomalies on the second factor score map (Figure 6.15) indicate the Cd affected samples are distributed all over the studied area. Positive anomalies are samples were OM and TN have an important contribution.

The group formed by samples 2.OG, 3. OG/RD, 4.RD, 6.RD and 13.PO in the scatter plot of the cases on the first factorial plan (Figure 6.17) doesn't seem to be affected by Cd, being more important the influence of general parameters and other PTM. It should be noted the opposite contribution of factor 1 on samples 14.PO and 11.RD, which have different texture characteristics (being the first one a silt loam soil and the second one a

sandy soil) indicating the influence of this property on PTM distribution. Moreover, they were found to be the samples with higher (14. PO) and lower (11.RD) contents of most metals, except for Cd.

The positive anomalies on factor 3 (Figure 6.16), can be identified as Hg affected samples with low C/N ratio. Negative anomalies are samples were C/N ratio is having a high contribution. The second factorial plan (Figure 6.18) shows the distribution of samples likely to be affected by the C/N ratio and the Hg concentration. It should be noted the position of samples 23, 24, 25 and 26, all agricultural sites with low C/N ratio.

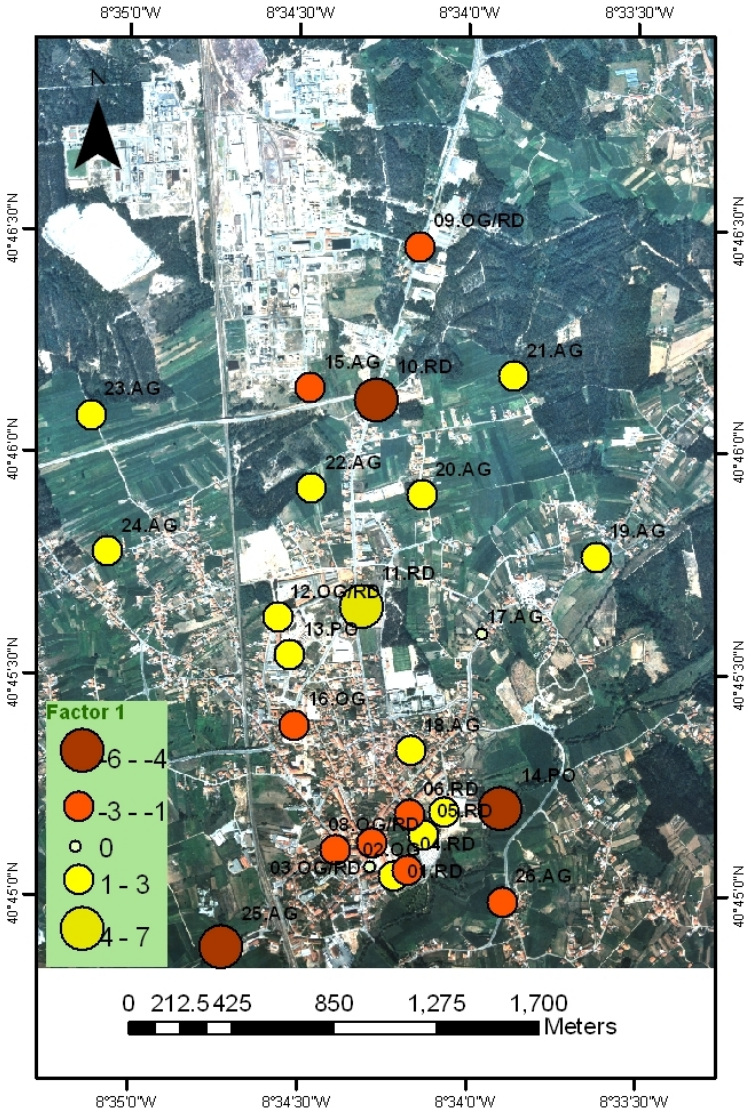


Figure 6.14 - Case contributions for the first factor (Fe, silt, Cr, Mn, Ni, Pb, Cu, Zn, OM, Hg and TN in opposition to sand).

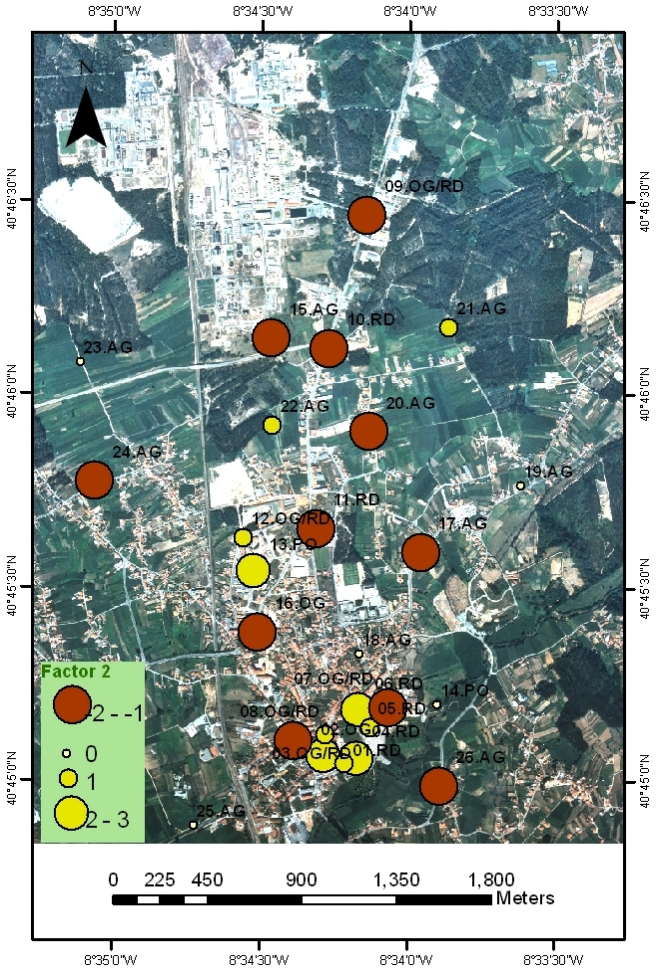


Figure 6.15 - Case contributions for the second factor (Cd in opposition to OM, TN).

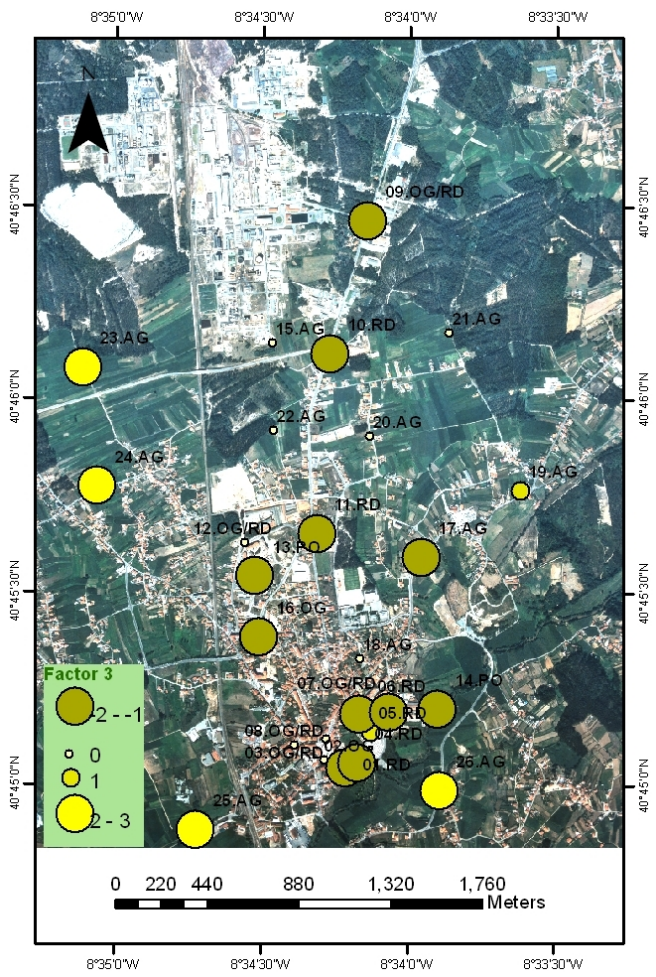


Figure 6.16 - Case contributions for the third factor (Hg in opposition to C/N).

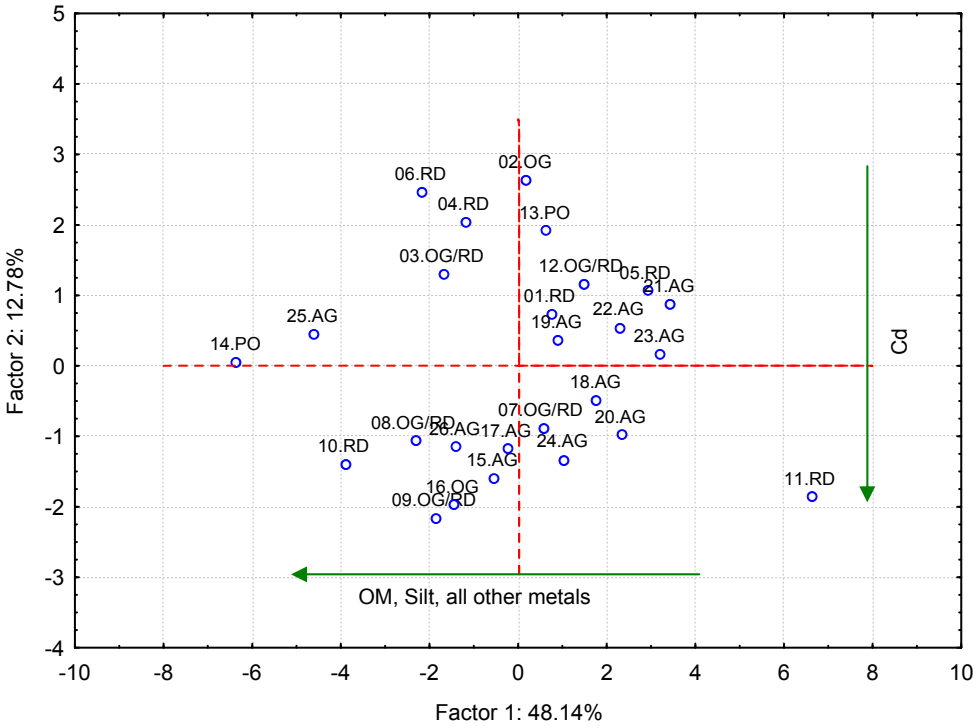


Figure 6.17 – Scatter of all sampling points plotted on the first factorial plane.

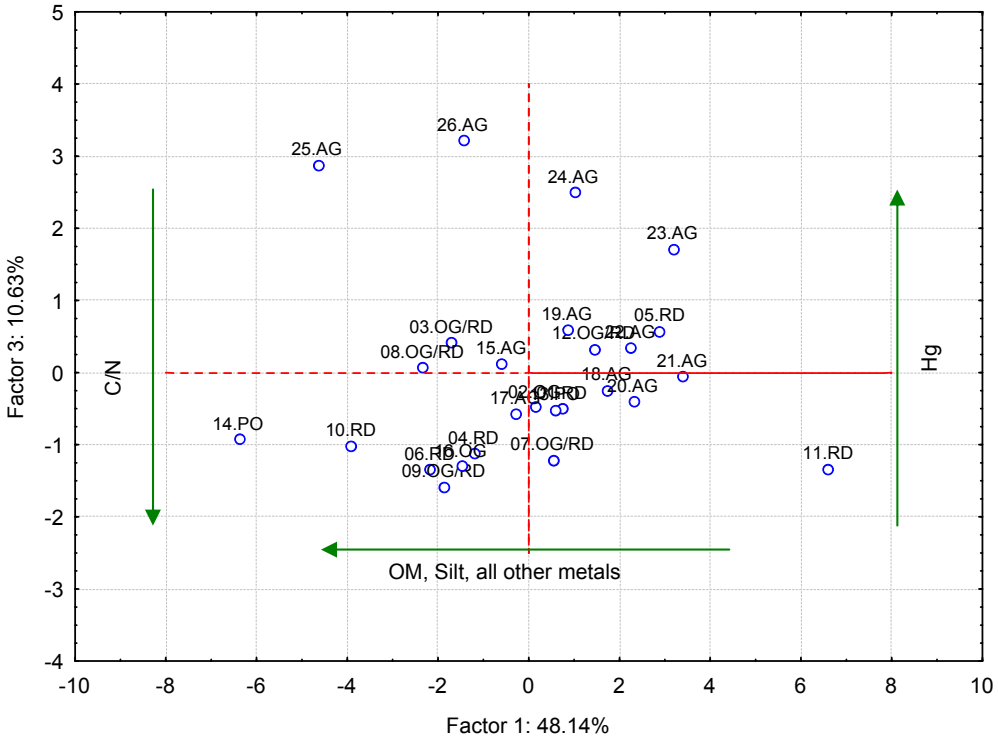


Figure 6.18 - Scatter of all sampling points plotted on the second factorial plane.

Figure 6.19 shows the scatter plot of cases for the third factorial plan, being the pH the only variable explained by the fourth factor. It's possible to observe which are the samples with lowest pH and high content on PTM and OM, and therefore identify samples that can represent an environmental menace.

The main conclusion from this PCA is the influence of "natural" features on the potentially toxic metal concentrations and their distribution. Parameters likely to affect PTM distribution are mainly OM, texture and pH.

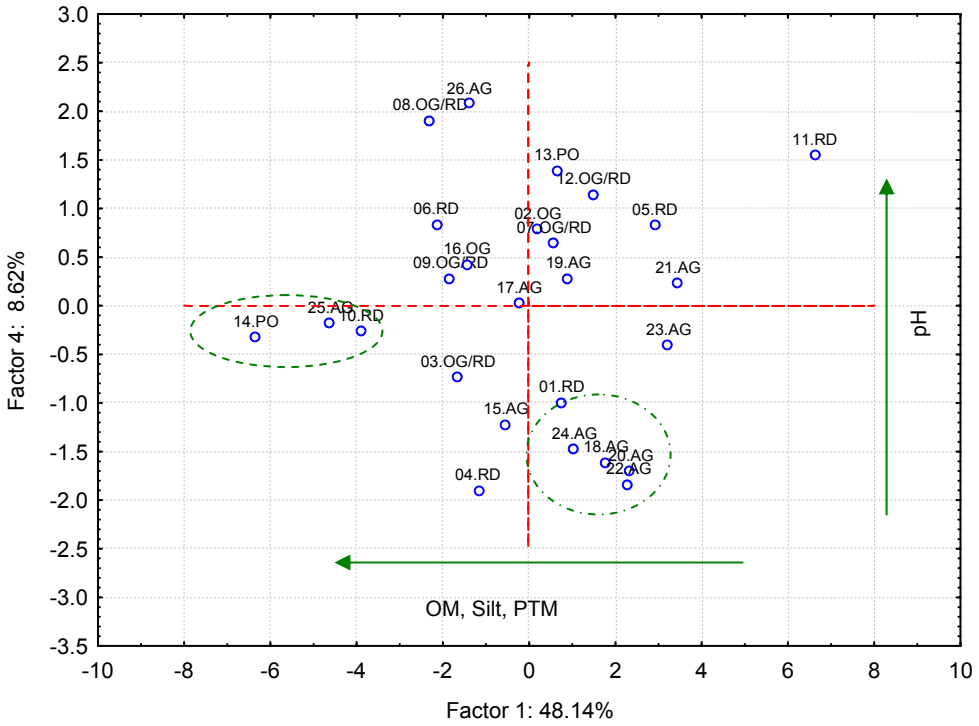


Figure 6.19 - Scatter of all sampling points plotted on the third factorial plane.

6.3.4 The land use influence and spatial distribution

Median PTM values for each land use are shown in Table 6.7. When performing the Kruskal-Wallis One Way Analysis of Variance on Ranks test to each metal, in order to find statistical differences from land uses, any difference could be proved. Despite this, Cu values were found to be higher in the RD samples, with a median value of 39 mg/kg. These samples are under the influence of a very busy road that crosses Estarreja, which during decades had high traffic intensity. The median value for AG is 23.6 mg/kg and for PA/OG is 45.0 mg/kg, however, excluding sample 14 this value falls to 19.8 mg/kg. Pb also showed differences between median values for RD (38.6 mg/kg), AG (34.2 mg/kg) and OG/PA (29.8 mg/kg). Cr also showed a high difference between median

concentrations in RD (22.6 mg/kg) and AG (8.6 mg/kg). This tendency, higher PTM concentrations in roadsides, is in accordance with other studies in urban soils (Paterson *et al.*, 1996), however the agricultural sites in Estarreja shows very high medians of PTM concentrations and the main reason should be that in this study agricultural sites are very close or inside the urban area and under influence of industry. On the other hand Zn has a higher median in AG (68.9 mg/kg) followed by RD (53.7 mg/kg). The same was observed for Hg, due to the hotspots found that are agricultural sites and therefore the median concentration for this land use is slightly higher than for the other land uses.

Table 6.7 - Median concentrations by land use.

Parameter	Land use			Total
	AG	OG/PO	RD	
Cu (mg/kg)	23.6	45.0	39.0	28.4
Pb (mg/kg)	34.2	29.8	38.6	34.7
Zn (mg/kg)	68.9	49.6	53.7	59.3
Mn (mg/kg)	114.6	201.5	147.3	146.3
Fe (%)	0.66	1.41	0.66	1.02
Ni (mg/kg)	8.1	12.4	8.6	8.5
Cr (mg/kg)	8.6	18.6	22.6	14.6
Cd (mg/kg)	0.46	1.26	1.17	0.61
Hg (mg/kg)	0.21	0.19	0.13	0.2

Cd showed a similar distribution over the study area, with the highest concentration found in a roadside, near the chemical complex (Figure 6.20). Moreover the highest concentrations can be observed in samples near the main road and in samples 25.AG and 14.PO, known to be severely contaminated.

The highest concentrations of Zn were found in samples 15.AG and 10.RD, both very close to the chemical complex (Figure 6.21). In addition both samples showed an enrichment factor of SF in relation to SB layer higher than 1.5, indicating an atmospheric deposition of Zn. Also sample 14.PO, has high concentration of this metal, as well as sample 25.AG, the one near the Esteiro of Estarreja. In fact, sample 14.PO shows the highest levels for all metals, except Hg, being the main source of pollution the river Antuã that often inundate this park. Antuã river is severely contaminated, mainly with Cu, Cr, Ni and Zn from industry situated upstream, being the discharges mainly from metalomechanics, untreated domestic sewage and textiles (Moreno, 2000).

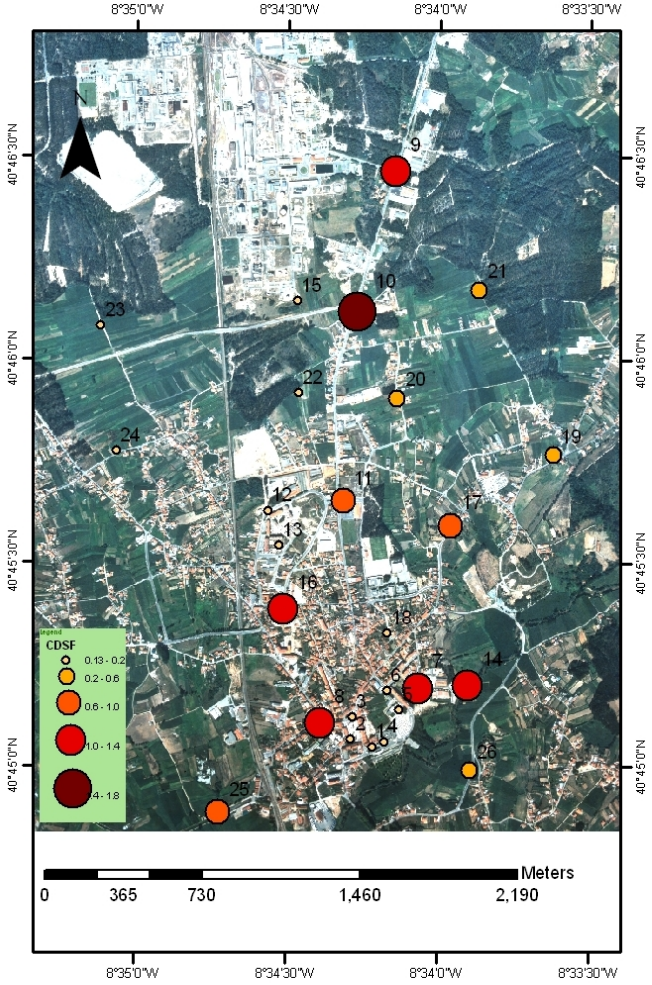


Figure 6.20– Spatial distribution of Cd in surface layer of Estarreja urban soils.

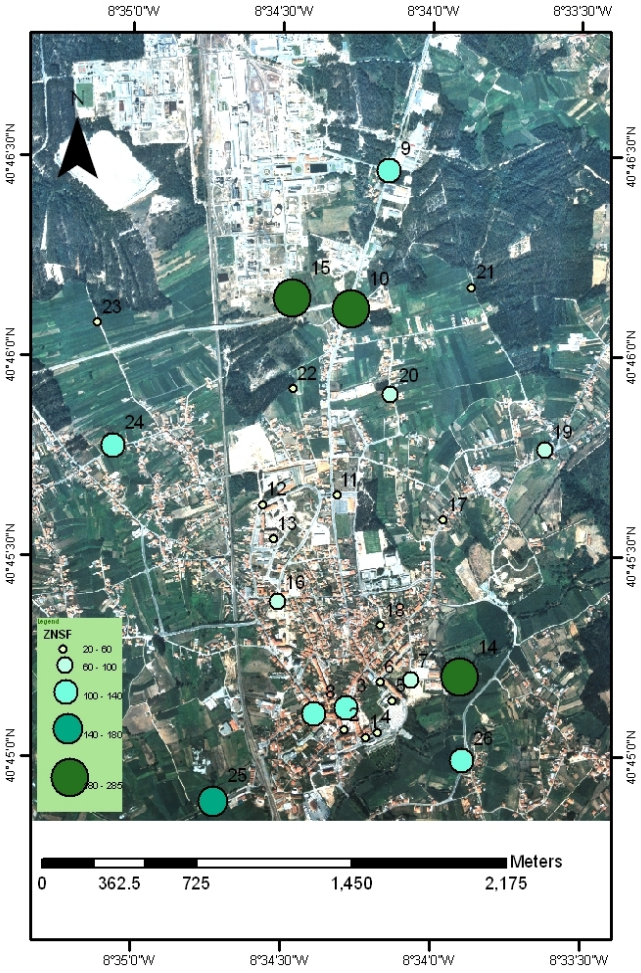


Figure 6.21– Spatial distribution of Zn in surface layer of Estarreja soils.

The highest concentrations of Hg were found in samples near the chemical complex (sample 15.AG) or near the "Esteiro the Estarreja" (sample 25.AG), a channel from the Ria de Aveiro lagoon where highly contaminated effluents from a chlor-alkali plant have been discharged from 1950's until 1994 (Figure 6.22). Also sample 24.AG showed a high concentration of Hg, being this site near a discharge point from the chemical complex during many years (Vala de S. Filipe). The source of Hg in sites 24.AG and 25.AG should be different from the samples 10.RD and 15.AG, located near the complex which showed an enrichment of the SF layer, indicating the atmospheric deposition of Hg (Figure 6.3).

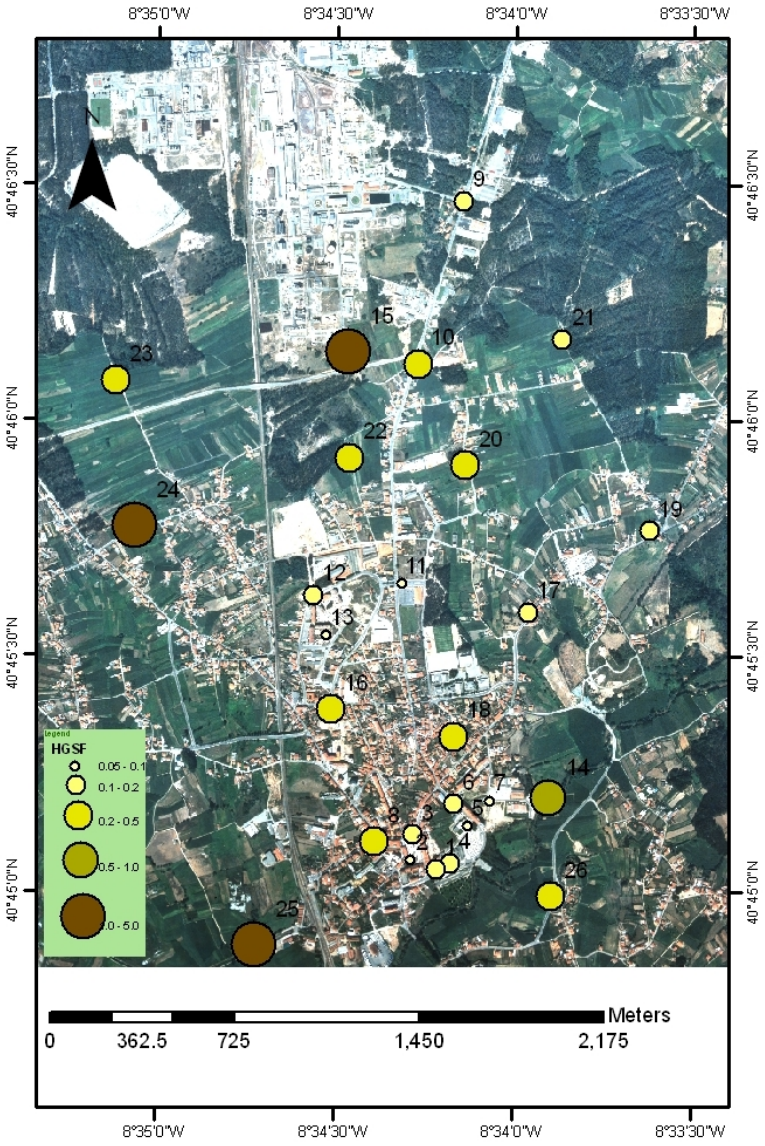


Figure 6.22– Spatial distribution of Hg in surface layer of Estarreja soils.

Cu and Pb seem to be more affected by diffuse pollution as a result of atmospheric deposition (Figure 6.23 and Figure 6.24). However, the Antuã river can also be considered a source of these metals (sample 14.PO). In the case of Pb, other point sources can also be addressed, being them the Esteiro of Estarreja (sample 25.AG) and a gas station near samples 1.RD and 4.RD. The spatial variability of these elements can be a result of different efficiency of soils samples to trap these pollutants due to their distinct characteristics (mainly texture).

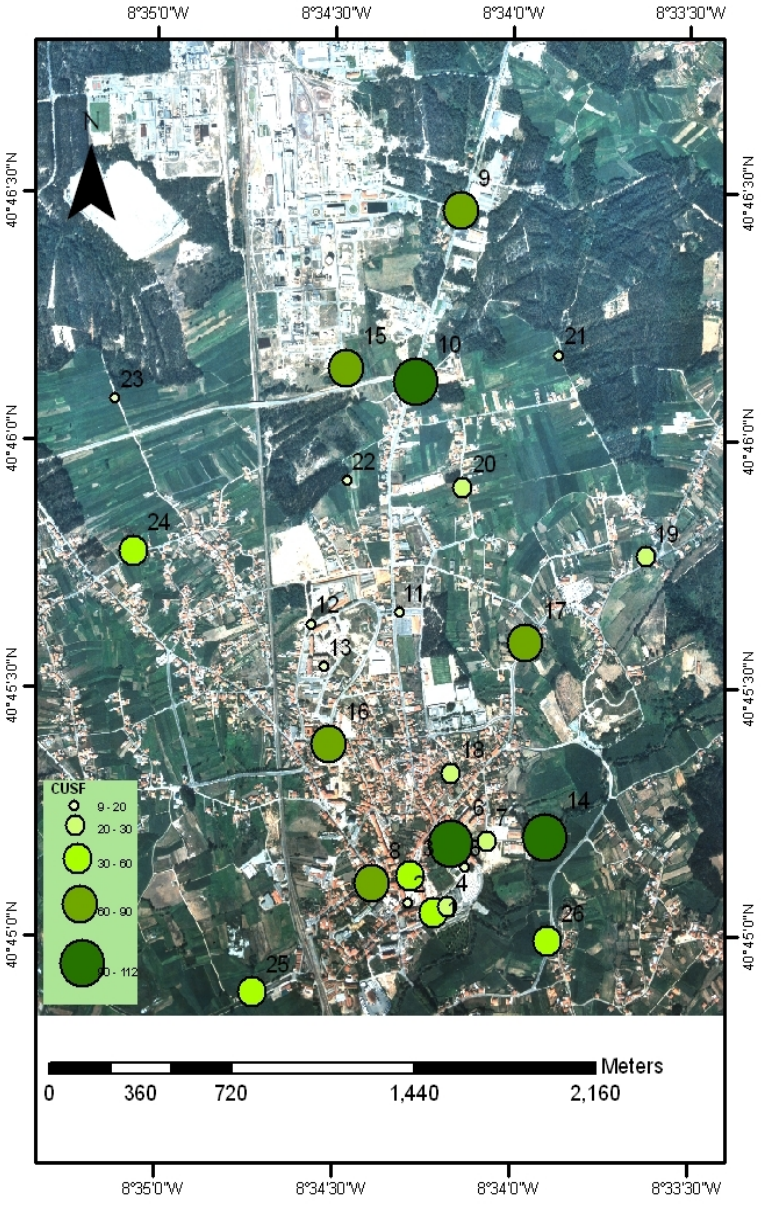


Figure 6.23 – Spatial distribution of Cu in surface layer of Estarreja urban soils.

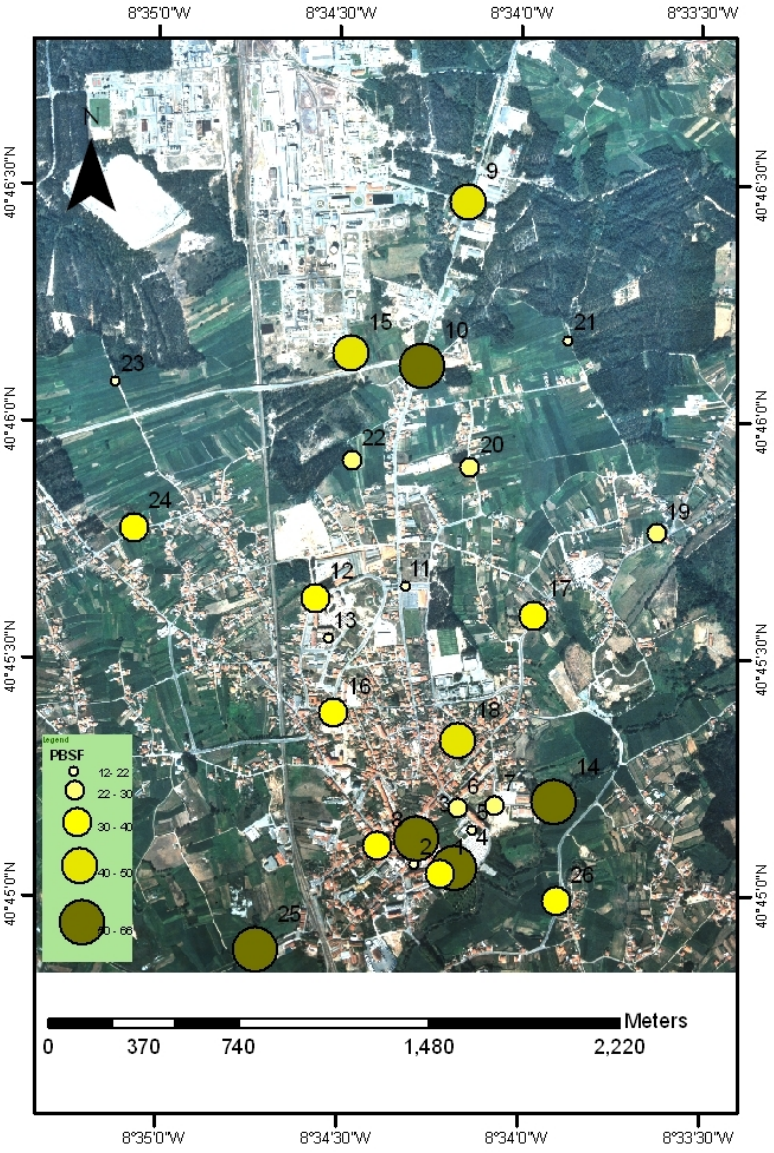


Figure 6.24 - Spatial distribution of Pb in surface layer of Estarreja urban soils.

Concluding, three sources of pollution to the urban soils of Estarreja can be defined: the Antuã river, emission of the chemical complex and the Esteiro of Estarreja. In the first case the discharges without any treatment is still an undergoing problem, and in the former one it is a result of decades of discharges. However natural features of soils have influence on PTM distribution, being difficult to assess the influence of industrial, urban or rural activities. Moreover the sampling area should be greater enough to notice the area under influence of pollution from the chemical complex.

6.4. Conclusions

Concentrations of potentially toxic metals in Estarreja soils are not very high, especially when compared with other cities. Nevertheless some sites showed high concentrations of PTMs, being some above guidelines values.

Hg, Zn, Cu and Pb seem to have an anthropogenic origin. Mercury is, however, the most evident case, especially when comparing with Aveiro and with other cities. The Hg contamination can be both from atmospheric deposition or contaminated channels where untreated effluents were released during decades. Cu and Pb showed highest median concentrations in roadsides showing however a uniform distribution over the study area, indicating diffuse pollution either due to traffic or industry. Therefore, levels of PTM in Estarreja soils can be assigned to the following origins: natural causes (Fe, Ni, Cr, Mn), industry effluents (Zn, Hg) and diffuse pollution from traffic or industry (Cu, Pb and Cd).

Nevertheless, concentrations of PTM will be dependent of pedo-lithological conditions, being difficult to compare with other locals with different parent materials. The parent material is a very important factor that will influence not only the natural concentrations but also the soil properties itself. For all metals (both the ones with recognized natural origin and the ones with anthropogenic origin), soil characteristics that influence the efficiency to trap and hold metals (e.g., soil texture and specially organic matter content) seem to control the distribution/levels in the study area. Results seem to prove that spatial variability of PTM levels is a very important indicator in the definition of soil quality in urban environments.

7. Determination of organic pollutants in Estarreja urban soils

7.1. Introduction

Two classes of compounds can be used as "tracers" of several activities: polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyl's (PCBs). Anthropogenic activities such as traffic, industry, domestic heating and agriculture can be major sources of these compounds. PAHs are by-products resulting from the incomplete combustion or pyrolysis of organic material such as coal, gas and oil, residential heating, traffic emissions, waste discharge and internal combustion engines (Wagrowski & Hites, 1997; IPCS, 1998; Mielke *et al.*, 2001; Rost *et al.*, 2002). Therefore, they are ubiquitous in urban environments and considered good markers of urban activities (Wong *et al.*, 2004). PCBs are normally associated with industry, particularly electrical industry.

PAHs are a large group of semivolatile, chemically stable and hydrophobic organic compounds, which have two or more fused benzenoid rings in their structure and no elements other than carbon and hydrogen (IPCS, 1998; Marce & Borrull, 2000). PCBs are chlorinated hydrocarbons with a biphenyl nucleus on which one to ten of the hydrogens have been replaced by chlorine. They were commercially produced as complex mixtures for a variety of uses, especially for electrical industry but also used in hydraulic fluids, as plasticizers in sealants, resins, waxes and paints as well as flame retardants in lubricating oils. The chemical properties that made them so useful for industry were low vapour pressures, low water solubilities, low reactivity, low degradability and high dielectric constants (Edgar *et al.*, 1999). Unfortunately, these properties are also responsible for the PCB environmental contamination problem.

Organic pollutants can be highly persistent in the environment, easily adsorbed to surfaces and accumulative through the food chain. Since some of them are known or suspected of carcinogenic and/or mutagenic activity, the fate of these compounds in the soil environment is critical to assess their potential hazard risk (Folch *et al*., 1996; Machala *et al.*, 2001). Persistent organic pollutants (POPs) are transported in the atmosphere over short and long distances in both gaseous and particulate forms and they tend to accumulate in soils where, due to their hydrophobicity, are likely to be retained for many years (Motelay-Massei *et al.*, 2004; Erickson, 1997). Dry and wet atmospheric deposition is the main input of semi-volatile organic compounds to soil. Consequently, soils constitute, even in the urban context, the main environmental compartment for accumulation of organic contaminants as they are particle reactive chemicals and highly lipophilic (Edgar *et al.*, 1999; Wong *et al.*, 2004). The contamination of the environment by toxic organic compounds can cause chronic disruption of the biological processes within

soil, particularly the ones related with soil organic matter dynamics which are key parts of the carbon and nitrogen cycles. Organic contaminants are known to be strongly retained in the organic phase of a soil and although they are subject to biodegradation and photodegradation, it is known that uptake of organics into soil organic matter can be virtually irreversible (Yang *et al.*, 2001). Moreover, kinetics depends on soil type, with slower rates observed for high-organic matter soil horizons (Girvin *et al*., 1993), being the distribution constants for organic contaminants in soil proportional to the soil organic carbon content (Paya-Perez *et al.*, 1991).

For all these reasons, the analysis of persistent organic pollutants has increasingly importance in environmental assessments. Therefore, testing and validating methods for assessing the presence and the quantification of organic pollutants in soils is a useful and important tool for urban planning.

7.2. Methodology for determination of PAHs and PCBs

7.2.1 Extraction and cleanup

The extraction procedure was adapted from the US EPA method 3500B (USEPA, 1996b) using a Soxhlet apparatus. Ten grams of soil (< 2mm fraction) were weighed and placed inside a pre-washed glass wool thimble in the extraction chamber and cleaned glass wool was used to avoid loss of soil to the extract. Samples were extracted for 8 hours using a high grade hexane/acetone mixture (2:1). The extracts were concentrated to a known volume using a rotative evaporator at 30ºC and preserved in hexane:acetone (2:1) at 4ºC in dark glass vials with Teflon seals and parafilm to avoid evaporation. Extracts were submitted to a neutral alumina clean-up and solvent changed to isooctane for PCBs and to dichloromethane for PAHs analysis. The dry weight was calculated and the analysed mass adjusted to each soil sample. Determinations were performed in the surface layer samples.

7.2.2 GC/MS analytical apparatus

This study was focused in the analysis of 19 PCBs (congeners 1, 5, 18, 31, 44, 52, 66, 87, 101, 110, 138, 141, 151, 153, 170, 180, 183, 187, 206) and 16 PAHs based on the US EPA list and using a modified 8270 Method for determination. The 16 PAHs determined were: Acenaphthene (ACE), Acenaphthylene (ACY), Anthracene (ANT), Benz(a)anthracene (BAA), Benzo(b)fluoranthene (BBF), Benzo(k)fluoranthene (BKF), Benzo(ghi)perylene (BGHI), Benzo(a)pyrene (BAP), Chrysene (CRY),

Dibenzo(ah)anthracene (DBAH), Fluoranthene (FLA), Fluorene (FLU), Indeno(1,2,3-cd)pyrene (IND), Naphthalene (NP), Phenanthrene (PHE), Pyrene (PYR).

Extracts were analysed using gas chromatography with mass spectrometry detection (GC/MS-QP5050A, Shimadzu Corporation), using helium as carrier gas and a DB-5 fused silica capillary column. The detection was achieved with a mass selective detector using electron ionization (EI) in the ion monitoring acquisition mode (SIM). The injection volume was 1 µl and in splitless injection mode using a liner with fused silica wool to promote complete vaporisation and also trap non-volatile residues. Column temperature for PCBs was programmed as follows: 40 ºC for 2 minutes, increased at a rate of 10 ºC /min until 290ºC and kept for 8 minutes. The column flow was 0.7 ml/min. The injector temperature was 280ºC and the interface temperature was 300 ºC. For the analysis of the 16 PAHs injector temperature was 290ºC and the interface temperature was 300 ºC. The column temperature was programmed as follows: 35 ºC for 2 minutes, increased at a rate of 10 ºC /min until 220ºC followed by 6ºC /min until 260ºC and finally at 3ºC /min until 300ºC and kept for 6 minutes.

7.2.3 Quality control and quality assurance procedures

For quality control assessment two sub-samples of each soil sample were extracted in duplicate. Replicate analysis of the soil samples gave an error $<\pm 10\%$. Analysis of method blanks every tenth sample was performed to detect possible interferences from the reagents, glassware and other processing hardware.

Internal standard (ISTD) was used to check the consistency of the analytical step e.g. injection volume, instrument sensitivity and retention times. The first two are adjusted by calibration using the ratio of peak area compared with that for the internal standard. As retention time marker, ISTD, is used to identify and quantify the relative retention times (RRT) of unknown peaks. Relative retention time of the sample component is with 0.06 RRT units of that of the standard component. For PCBs determination the ISTD used was PCB congener 209 and for PAHs determination a deuterated PAHs mixture. ISTD was added to each sample prior to GC-MS analysis.

Concentration of each compound was determined by using an internal standard multipoint calibration curve using five concentration levels (from 5 to 60 µg/l for PCBs and from 25 to 500 µg/l for PAHs). The composite stock solutions were obtained by diluting commercial prepared stock standards (purchased from Supelco) in isooctane (for PCBs) or in dichloromethane (for PAHs) and standards were then prepared in the same solvents.

In order to evaluate the linearity of the calibration the relative standard deviation was calculated based on the response factor (RF). The relative standard deviation of the response factors (RSD), for each analyte in the calibration curve, was always bellowi 20%. The limit of detection (LOD) (in pg/µl) for each analyte was estimated from the calibration curve as the concentration giving a blank signal, plus three standard deviations of the blank (Table 7.1 and Table 7.2).

Table 7.1 - List of PCBs selected for analysis, their retention time (minutes), m/z and estimated limit of detection (LOD) (pg/µl).

Analyte	IUPAC #	Retention Time (min)	Quantification ion	Confirmation ion	LOD (pg/µl)
2-Chlorobiphenyl	1	17.8	188	152;190	1.6
2,3-Dichlorobiphenyl	5	20.3	222	152;224	2.1
2,2',5-Trichlorobiphenyl	18	21.3	256	186;221	1.5
2,4',5-Trichlorobiphenyl	31	22.3	256	186;260	1.9
2,2',5,5'-Tetrachlorobiphenyl	52	23.1	292	220;150	3.4
2,2',3,5'-Tetrachlorobiphenyl	44	23.5	292	220; 255	3.2
2,3',4,4'-Tetrachlorobiphenyl	66	24.4	292	220;110	2.5
2,2',4,5,5'-Pentachlorobiphenyl	101	24.9	326	254;127	3.1
2,2',3,4,5'-Pentachlorobiphenyl	87	25.5	326	254;127	3.6
2,3,3',4',6-Pentachlorobiphenyl	110	25.7	326	254;184	3.6
2,2',3,5,5',6-Hexachlorobiphenyl	151	25.9	360	290;144	2.8
2,2',4,4',5,5'-Hexachlorobiphenyl	153	26.6	360	290;363	2.6
2,2',3,4,5,5'-Hexachlorobiphenyl	141	26.9	360	290;145	2.7
2,2',3,4,4',5'-Hexachlorobiphenyl	138	27.2	360	290;145	3.5
2,2',3,4',5,5',6-Heptachlorobiphenyl	187	27.5	394	162;324	3.2
2,2',3,4,4',5',6-Heptachlorobiphenyl	183	27.7	394	324;162	3.4
2,2',3,4,4',5,5'-Heptachlorobiphenyl	180	28.7	394	324;162	3.3
2,2',3,3',4,4',5-Heptachlorobiphenyl	170	29.4	394	324;162	3.0
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	206	32.6	464	392;196	1.3

Acquisition was performed using one quantification ion and two confirmation ions. Ions monitored were selected following the criteria of highest relative abundance, characteristic fragment ions and no interferences with the nearby peaks. PAHs and PCBs in real samples were identified when the chromatographic peaks coincide at same retention time with the standard, if quantification and confirmation ions are identified (Table 7.1 and Table 7.2) and the ratio between the ions were the same in both sample and calibration mix (tolerance of 15%).

Table 7.2 - List of PAH selected for analysis, their retention time (minutes), m/z and estimated limit of detection (LOD) (pg/µl).

Analyte	Retention Time (min)	Quantification ion	Confirmation ion	LOD (pg/µl)
NP	12.9	128	102; 51	13.2
ACY	13.0	152	151;76	10.6
ACE	17.1	154	152;76	8.9
FLU	17.5	166	165;82	16.8
PHE	17.6	178	176;86	11.6
ANT	18.9	178	176;89	16.7
FLA	21.5	202	101;200	15.9
PYR	21.5	202	101;200	14.6
BAA	21.7	228	226;114	7.4
CRY	25.2	228	226;113	11.7
BBF	26.0	252	125; 253	13.3
BKF	30.7	252	126;250	13.5
BAP	30.8	252	126;253	15.2
IND	30.9	276	138;277	18.5
DBAH	36.0	278	139;279	36.8
BGHI	36.1	276	138;227	16.4

Recoveries were checked by analysing five replicates of the LGC 6113 certified contaminated site soil (LGC®, UK) for PCBs (Table 7.3), two replicates of the LGC 6140 certified contaminated site soil (LGC®, UK) and three replicates of the CRM124 -100 (RTC, USA) for PAHs (Table 7.4). The RSD was bellow 10% for each analyte. Recoveries ranged from 69 to 108 % for PCBs and from 26 to 105 % for PAHs. The low recoveries observed for some PAHs may be due to the fact of the reference material be quite old, especially the LGC 6140, and therefore the most volatile compounds were lost as in

previous works recoveries between 80-110 % were achieved. Moreover, as extracts are dried to solvent exchange, some volatile compounds may also be lost during this step. All results were included and any correction for recovery was made.

Table 7.3 - Average concentration (µg/kg) and recovery (%) of PCBs' present in the LGC 6113 reference material.

PCB Congener	LGC 6113 (µg/Kg)	Uncertainty* (µg/Kg)	Recovery (%)
52	11	3	105
101	23	6	72
138	43	13	103
153	42	12	69
180	29	8	108

* Defined in reference as the half width of the 95% confidence interval

Table 7.4 - Average concentration (mg/kg) and recovery (%) of PAHs present in the LGC 6140 and CRM 124 reference material.

Analyte	LGC 6140 (mg/kg)	Uncertainty (mg/kg)	Recovery (%)	CRM 124 (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
NP	3.9	0.5	40	8.71	1.02	26
ACY	10	4	30	6.63	0.48	54
ACE	- **		-	5.35	0.36	67
FLU	5.3	1.2	49	8.6	0.6	60
PHE	123	36	85	6.45	0.38	76
ANT	10.7	3.1	36	2.64	0.17	54
FLA	89	24	92	5.59	0.24	85
PYR	93	22	82	3.61	0.30	80
BAA	30	7	59	2.23	0.14	96
CRY	36	10	89	3.51	0.28	105
BBF	22	6	100	-**	-	-
BKF	20	6	81	6.93	0.42	63
BAP	7.1	2.2	46	5.72	0.37	64
IND	16.8	7.0	84	-**	-	-
BGHI	17.1	6.0	69	4.46	0.38	78

* Defined in reference as the half width of the 95% confidence interval
** These analytes do not exist in the certified reference material.

7.3. Results and discussion

Annex V shows individual results of PCB congener and PAHs concentration, in Estarreja samples and the Normality test (Kolmogorov-Smirnov test), performed with SPSS® 11.0. As not all parameters follow a normal distribution, non-parametric statistics was used. Principal Component Analysis (using STATISTICA® 6.0 software) was used to identify relationships between variables, after log transformation of the original data. Finally, the influence of the land use was studied by using the Kruskal-Wallis One Way Analysis of Variance on Ranks test.

7.3.1 PCBs distribution in Estarreja urban area

Table 7.5 shows the results of the sum of the 19 PCB congeners analysed. The median content of total PCBs in Estarreja urban soils was 8.8 µg/kg with a range between 2.3 and 55.2 µg/kg. Besides sample 18.AG, that has a very high content in total PCBs, the highest values were found in samples 3.OG/RD, 14.PO, 15.AG, 16.OG, 20.AG and 25.AG. The spatial distribution of PCB concentrations (Figure 7.1) seems homogeneous over the sampling area, indicating diffuse pollution from atmospheric deposition, however it should be noted that some of the samples with higher concentrations are in agreement with metal's concentrations.

Table 7.5 – Sum of the 19 PCBs analysed for each sample and of the 6 from the European norm (18, 52, 101, 138, 153, 180) (µg/kg).

Sample	∑19PCBs	∑6PCBs	Sample	∑19PCBs	∑6PCBs
01.RD	2.5	1.1	**13.PO**	4.7	0.8
04.RD	9.1	1.2	**14.PO**	16.2	6.0
05.RD	4.6	1.2	**15.AG**	15.5	6.4
06.RD	6.7	1.7	**17.AG**	9.3	2.8
10.RD	6.3	2.2	**18.AG**	55.2	29.9
11.RD	2.3	0.6	**19.AG**	10.7	3.7
03.OG/RD	15.6	7.6	**20.AG**	15.2	7.3
07.OG/RD	9.6	2.6	**21.AG**	8.4	4.2
08.OG/RD	6.1	1.9	**22.AG**	4.7	1.9
09.OG/RD	5.9	2.3	**23.AG**	11.2	2.5
12.OG/RD	12.9	2.8	**24.AG**	6.4	2.3
02.OG	4.7	1.7	**25.AG**	14.5	4.7
16.OG	17.3	3.8	**26.AG**	8.4	3.5

These values were found to be low, for an urban area, when compared with previous studies. For example, Lead *et al.* (1997) reported concentrations of 20 to 30 µg/kg in different long term agricultural soils, 17.5 µg/kg in south Norway and 9.5 µg/kg in north Norway. It has been reported in rural and urban areas of some countries the following values (ISS, 2003; Covacia *et al.*, 2001): in Belgium from 3.8 to 39.3 µg/kg (mean value of 14.5); in Italia from 3.8-91.0 µg/kg (mean value of 11); in Greece a mean value of 3.5 µg/kg; and in Romania values from 1.0 to 134 µg/kg (mean value of 35.0). In Seine River Basin the sum of 7 PCBs was found to be from 0.09 µg/kg (town centre, 12,175 inhabitants) to 159 µg/kg (town centre, 8,000 inhabitants, northeast of an industrial area), both in public gardens (Montelay-Massei *et al*., 2004). However Estarreja results are above the mean value of 4 µg/kg (sum of 30 PCBs) in UK soils reported by Lead *et al.* (1997).

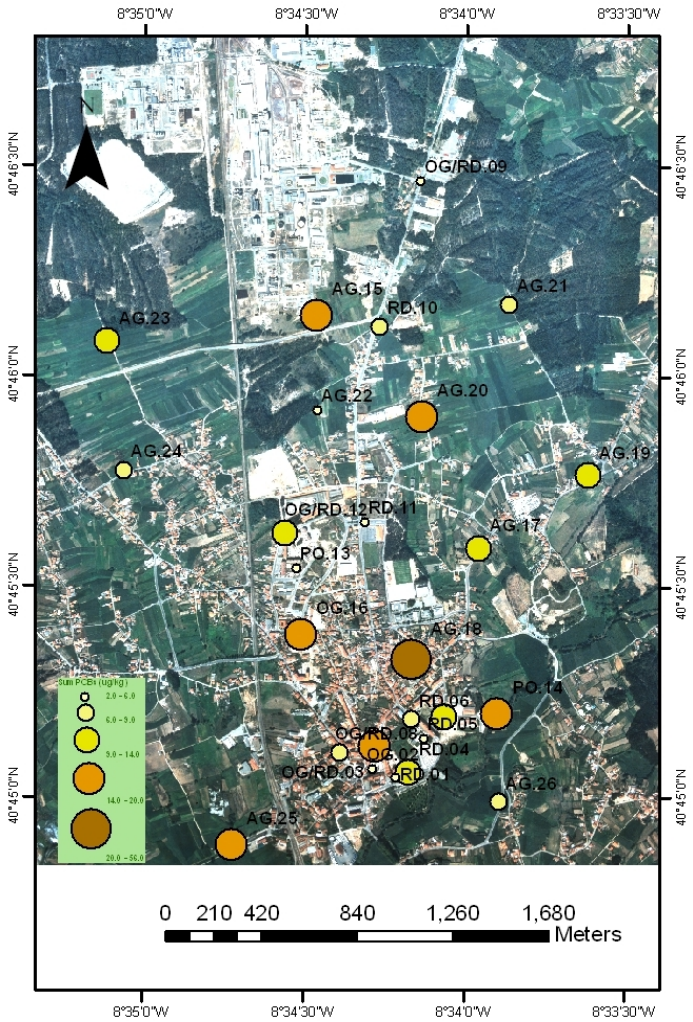


Figure 7.1 – Spatial distribution of PCBs (Σ19PCBs) in surface layer of Estarreja urban soils.

Although the magnitude of values observed in many studies, the Italian legislation has a limit value of PCBs in soils from residential areas/public land of 1 μg kg^{-1} (sum of total PCBs) what seems to be very low. In the Dutch guidelines it is established that the optimum value, given as the sum of 7 PCBs (18, 52, 101, 118, 138, 153 and 180) from the European Standard, is 20 μg/kg. In this case, as only six of those seven PCBs were studied, it was considered the sum of these 6 PCBs (18, 52, 101, 138, 153 and 180) and only sample 18 was above this value. Sample 18 is an agricultural soil near the town centre, and there is no apparent reason for this high concentration observed.

No statistical differences between land uses could be observed, however the highest median concentration was found in agricultural sites (10.7 μg/kg) and the lowest one in roadsides (5.4 μg/kg).

7.3.1.1 PCB congener pattern in soil

The PCB profiles can give some indications about the origin and the fate of these contaminants. Therefore, the median percentages of the individual congeners of Σ19PCBs were calculated (Table 7.6). In general, lower-chlorinated (<3Cl) PCBs are in less percentage than the higher–chlorinated (>4Cl) ones. The profile of Estarreja is dominated by hexa-chlorinated congeners (PCBs 138, 141, 151, 153) consistent with results in the literature for remote sites (Lead *et al.*, 1997; Weiss *et al.*, 2000).

In spite of the results obtained, the industrial sites are usually characterized by homogeneous proportions (as many light compounds as heavy ones) with slightly higher proportions of the higher molecular weight PCBs, indicating that the PCBs signature is preserved over short transport distance. The principal elimination pathway of PCBs from soil is volatilisation (Montelay-Massei *et al.*, 2004), with the air-soil system approaching a thermodynamic equilibrium, being this process that affects mainly the lightest congeners. Wilcke *et al.* (1999) has concluded that, lower chlorinated PCBs become more dominant the more distant from the sources, because of their volatility. Other studies (Wilcke *et al.,* 1999; Weiss *et al.*, 2000) show that lower chlorinated PCBs are mainly dominant in the rural soils or remote sites. PCBs with 5 or more chlorines are quite resistant to biodegradation, but photolysis may result in some breakdown of highly-chlorinated PCBs.

There is a range of possible explanations for this PCB profiles (Wilcke *et al.*, 1999) being in this case the most probable the age of the contamination (which determines the time available for volatilisation) and sample treatment (as drying extracts may lead to PCB losses, particularly of the more volatile lower chlorinated congeners).

Table 7.6 - Median percentage of PCB congeners Estarreja soils.

PCB Congener	(%)	Group	(%)
1	3.67	CB	3.67
5	3.56	Bi-CB	3.56
18	3.38	Tri-CB	9.08
31	5.77		
52	5.05		
44	1.47	Tetra-CB	8.25
66	2.21		
101	2.88		
87	1.02	Penta-CB	6.88
110	1.86		
151	4.77		
153	11.08	Hexa-CB	36.62
141	11.37		
138	8.13		
187	3.13		
183	1.29	Hepta-CB	16.05
180	4.51		
170	3.51		
206	7.82	Octa-CB	7.82

PCA was performed to investigate the spatial differences and similarities of congener patterns in soil samples from different sampling sites. Concentrations obtained from chemical analysis for the 19 compounds were log transformed and therefore the initial matrix was constituted by 26 individuals and 19 variables. In this way, the 19 eigenvalues extracted by PCA for log data are presented in Figure 7.2. Table 7.7 shows the factor loadings (with the ones higher than 0.5 marked in bold), eigenvalues and percent of variance for the first four factors with eigenvalues higher than unit, which explain by themselves 74% of total variance. Projections of the variables in the first factorial plan, defined by axis 1 and 2, are shown in Figure 7.3. Projection of the cases on the first factorial plan is shown in Figure 7.5.

By observing Table 7.7 and Figure 7.3, where the projection of the first factorial plan is represented, it's possible to conclude that the first factor its loaded by the PCB congeners 138, 153, 110, 151,180, 170, 141, 87, 101, 44, 206, 52, 18, 187. On other hand, the second factor its loaded by the PCB congeners 31, 5, 52 in opposition to 183. The third factor is loaded by the PCB congener 187 and the fourth factor by PCB congeners 1 and 141. These last two factors are not represented as their contribution is not very significant.

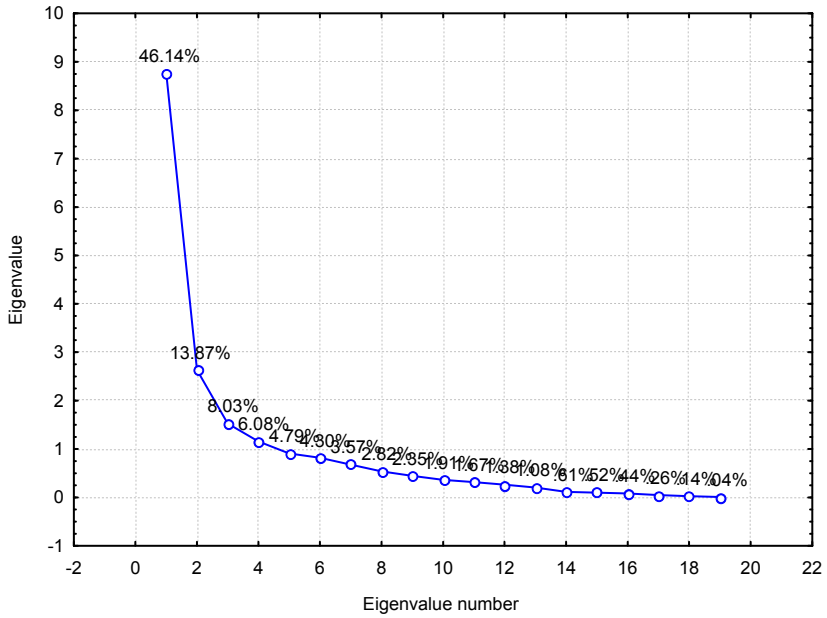


Figure 7.2 – Scree plot showing the 19 eigeinvalues.

Table 7.7 – Factor loadings, eigenvalues and percent of variance for the first four factors.

PCBs	Factor 1	Factor 2	Factor 3	Factor 4
1	-0.420227	-0.410472	0.332515	**0.542064**
5	-0.383593	**-0.562108**	0.247928	-0.337655
18	**-0.647234**	-0.479022	-0.391072	-0.062112
31	-0.291230	**-0.592495**	-0.163939	0.145483
52	**-0.654681**	**-0.544749**	-0.287760	-0.030156
44	**-0.691955**	-0.448371	-0.013746	-0.272819
66	-0.478176	-0.437464	0.024523	0.005821
101	**-0.715191**	0.060109	0.047822	-0.270800
87	**-0.717351**	0.002940	0.200024	-0.260011
110	**-0.854032**	0.220430	0.226251	-0.125006
151	**-0.848629**	0.176861	0.242724	-0.157950
153	**-0.864196**	0.271511	0.245300	0.149455
141	**-0.735043**	0.057087	-0.133973	**0.529555**
138	**-0.886435**	0.240310	0.292884	0.074082
187	**-0.565519**	0.367034	**-0.587090**	-0.045670
183	-0.449982	**0.544194**	-0.370521	-0.270417
180	**-0.844421**	0.245199	0.283918	0.025202
170	**-0.753103**	0.395660	-0.224573	0.269693
206	**-0.672483**	-0.124539	-0.401069	0.097166
Eigenvalue	8.77	2.64	1.53	1.16
% Total	46.14	13.87	8.03	6.08
Cumulative	46.1	60.0	68.0	74.1

The factorial plan defined by the first two axes contains 60% of the total information of the correlation matrix, explaining 17 of the 19 variables (Figure 7.3). By observing the projection of variables on the first factor plan it's possible to distinguish two groups characterized by the number of chlorines in the structure. Therefore one group is constituted by the light PCBs (1, 5, 18, 31, 44, 52 and 66) and the other by the penta-CB to the octa-CB.

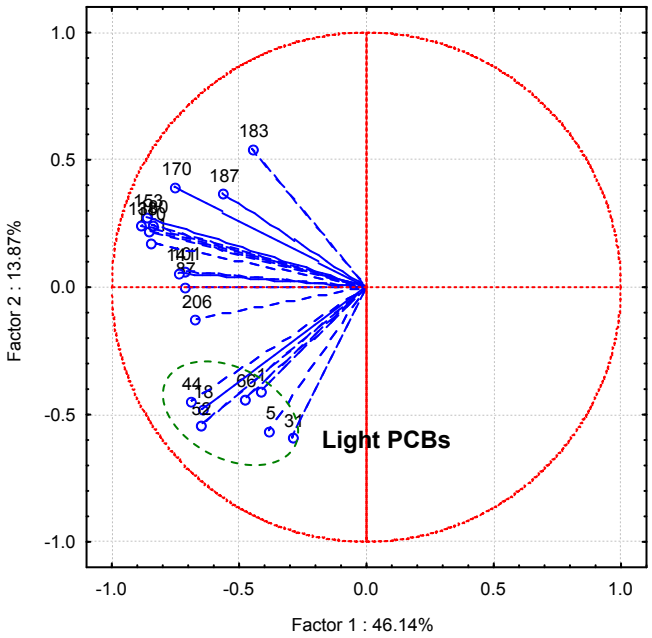


Figure 7.3 - Projection of the variables on the first factorial plane.

Distribution of factor-scores for the first factor (explained variance of 46%) is given in Figure 7.4, indicating the relative strength of this factor in each sample. Conceptually, factor 1 condenses the information of PCBs (mainly the penta-CB to the octa-CB) as tracers of long-term pollution.

When looking to the projection of cases on the first factorial plan (Figure 7.5) the main conclusion is that a distinction can be made within samples with higher content of more chlorinated PCBs. Samples 3.OG/RD, 4.RD and 24.AG are strongly affected by these PCBs but especially by PCB 183. This can be an indication of long term pollution. Sample 18.AG is the most contaminated one and is affected by the penta-CB to the octa-CB PCBs, with lower influence of the lighter PCBs. In fact this sample can be influencing the results as it is an outlier in what concerns PCBs concentrations. Samples 14.PO, 15.AG, 16.OG, 20.AG and 25.AG have a more homogeneous distribution of congeners probably

reflecting a more recent contamination. Moreover, some of these samples are located close to the chemical complex, which is the suspected source of these pollutants as they are byproducts of the PVC and polymers production. However further investigation is needed in order to address whether the chemical complex is a source or not of PCBs into Estarreja soils. On the other hand samples, 12.OG/RD, 19.AG, 7.OG/RD and 8.OG/RD have a strong contribution of lighter chlorinated PCBs. Sample 19.AG is outside the urban area but the other are located near the city centre.

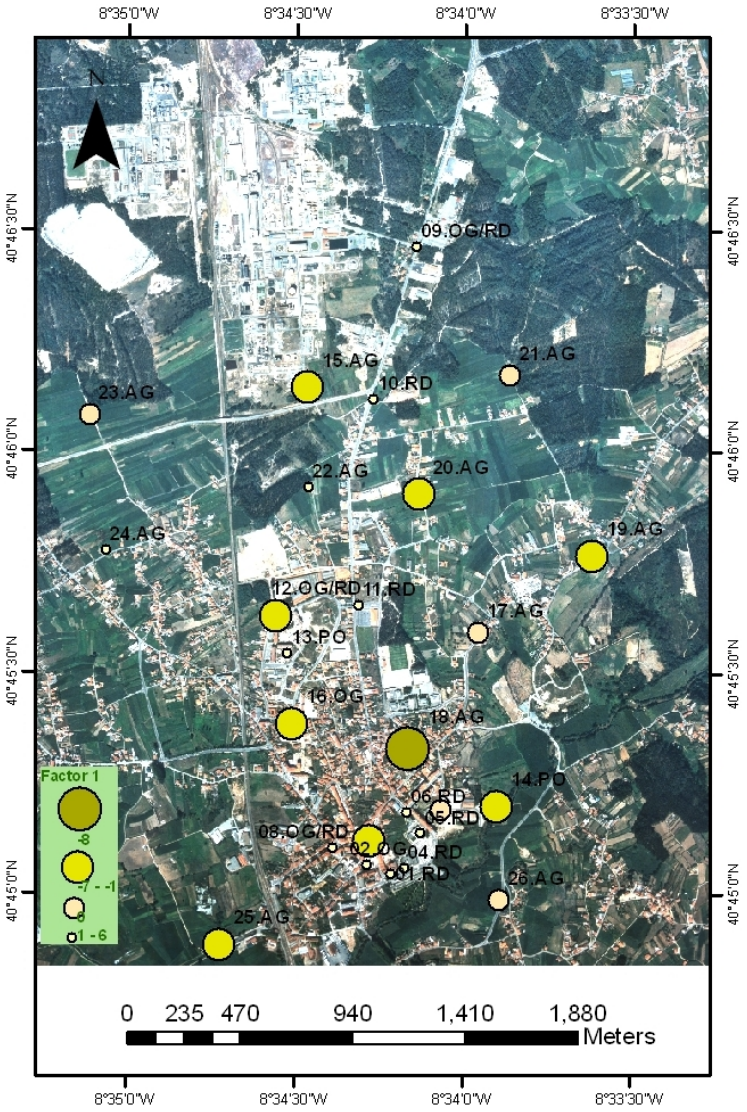


Figure 7.4 - Distribution of factor-scores for the first factor (congener 18, 52, 44, 101, 87, 110, 151, 153, 141, 138, 187, 180, 170 and 206).

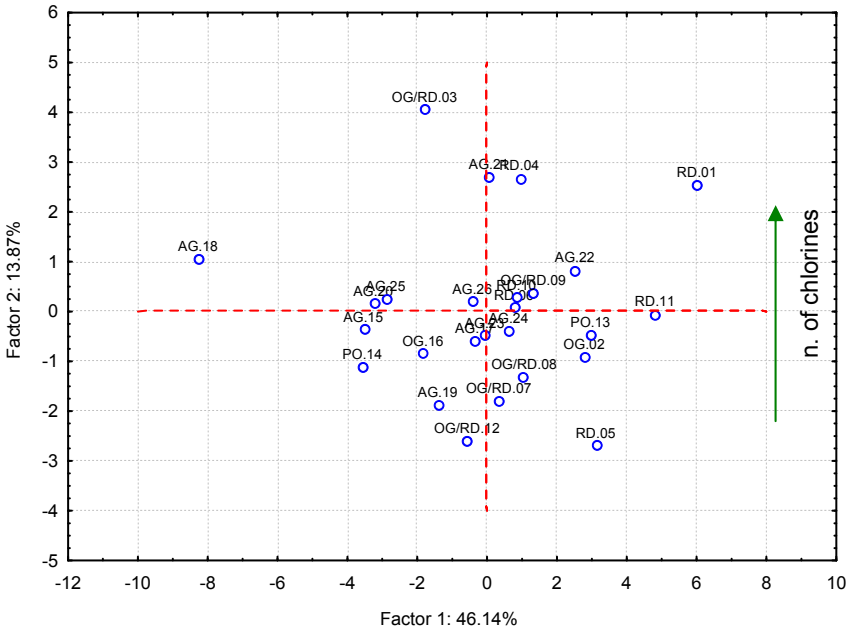


Figure 7.5 - Projection of the cases on the first factorial plan.

7.3.2 PAHs distribution in Estarreja urban area

Table 7.8 shows the sum of the 16 PAHs for each sample and in Figure 7.6 it is shown the spatial distribution of results. The sum of PAHs ranged from 26.7 to 2016 µg/kg with a median value of 97.5 µg/kg. The samples containing higher concentration of PAHs are samples 19.AG and 20.AG located outside the town, however samples 3.OG/RD and 4.RD also have high concentrations and they are located inside the town centre.

Table 7.8 – Sum of the 16 PAHs (ΣPAHs) analysed for each sample (µg/kg).

Sample	∑PAHs	Sample	∑PAHs
01.RD	63.5	**13.PO**	26.9
04.RD	525.2	**14.PO**	127.7
05.RD	42.3	**15.AG**	67.3
06.RD	45.7	**17.AG**	311.9
10.RD	119.9	**18.AG**	100.7
11.RD	50.4	**19.AG**	1121.3
03.OG/RD	495.7	**20.AG**	2016.2
07.OG/RD	49.2	**21.AG**	34.4
08.OG/RD	53.0	**22.AG**	41.1
09.OG/RD	71.6	**23.AG**	111.4
12.OG/RD	94.9	**24.AG**	52.3
02.OG	126.1	**25.AG**	117.4
16.OG	100.2	**26.AG**	148.8

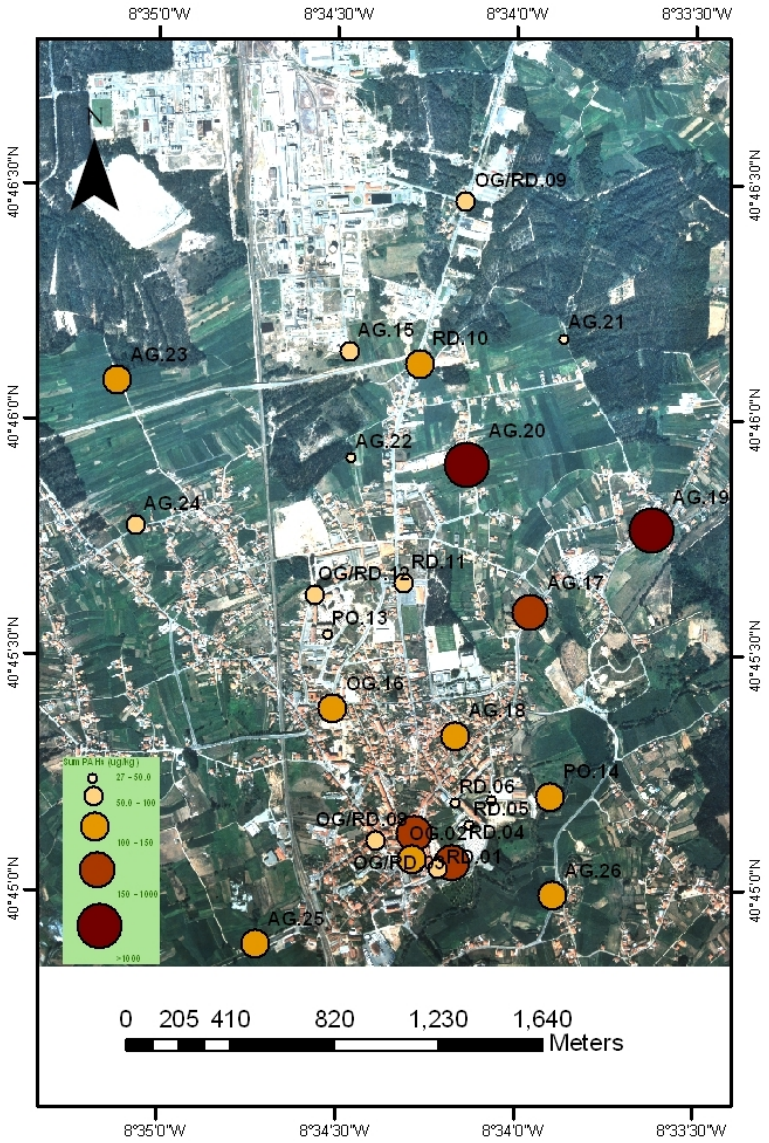


Figure 7.6 - Spatial distribution of SumPAHs in surface layer of Estarreja urban soils.

The concentration of PAHs in Estarreja soils is comparable with soils of other European cities (Trapido, 1999; Maliszewska-Kordybach, 1996; Motelay-Massei *et al.*, 2004). In Parnu (51 800 inhab., Estonia) PYR and FLU are the most abundant in both urban and suburban surface soils, where PAHs concentrations ranged from 49 to 2540 µg/kg (Maliszewska-Kordybach, 1996) and in Rouen (579 000 inhab., France) concentrations ranged from 5-292 µg/kg (Motelay-Massei *et al.*, 2004). Typical background concentrations of PAHs in European remote or agricultural sites have been estimated to be approximately 100 µg/kg (Trapido, 1999). Aamot *et al.* (1996) found concentrations in Norwegian surface forest soils ranging from 13 to 169 µg/kg and concentrations in agricultural soils in Poland showed average values of 264 µg/kg

(Maliszewska-Kordybach, 1996). The accumulation of PAHs in urban soils over many years could explain concentrations measured in the larger and older European cities where domestic heating and automobile traffic are the important potential sources of PAHs while in Estarreja the predominant potential source of these compounds should be industry due to its fairly short history and a low population.

According to Maliszewska-Kordybach (1996) PAH classification for agricultural soils, 21 samples from Estarreja can be considered as non-contaminated, since ΣPAHs were below 200 (µg/kg soil). On the other hand samples 19.AG and 20.AG can be considered heavily contaminated since they showed a ΣPAHs above 1000 (µg/kg soil). Samples 3.RD, 4.RD and 17.AG are considered weakly contaminated (ΣPAHs between 200 and 600 µg/kg). Although this classification was established for agricultural soils implying a more sensitive use of soil it has been used previously to classify soil samples taken from industrial and urban locations based on SumPAHs (Motelay-Massei *et al.*, 2004).

No statistical differences between land uses could be observed, however the highest median concentration was found in agricultural sites (111 µg/kg with a important contribution of the high levels of samples 19 and 20) and the lowest one in roadsides (57 µg/kg).

7.3.2.1 PAH pattern in soil

Usually the highest molecular weight PAHs are predominant in soils since the lighter ones are more easily biodegraded and volatilised (Wilcke *et al.*, 1996; Blanchard *et a*l., 2004). Because of that and also due to analytical problems, NP is below the detection limit in many samples. This compound is commonly associated with natural and not so much with anthropogenic processes (IPCS, 1998). The relative abundance of individual PAH in Estarreja soils is shown in Table 7.9, being the most abundant FLA and PYR followed by BBF and CRY. These PAHs are the ones usually associated with the combustion of fossil fuel and other burnable materials (IPCS, 1998) and this composition is typical for topsoil of European industrialized countries (Krauss & Wilcke, 2003).

PAHs originating from pyrolytic processes such as fuel combustion in automobiles are characterized by low PHE/ANT ratios (<10). On the other hand, petrogenic PAHs, formed by the slow maturation of organic matter, typically show higher PHE/ANT ratios (>10). Similarly, a ratio of 1 for FLA/PYR can also be indicative of pyrolytic origin of the PAHs (Wang *et al*., 2004; Tang *et al*., 2005).

In Estarreja the median ratio for PHE/ANT was 3.17 (ranging between 1.18 to12.3) and 1.16 for the ratio FLA/PYR (ranging between 0.88 to 1.53), both indicative of predominant pyrolytic origin of PAH such as motor vehicle exhaust.

When considering the sum of the 6 carcinogenic PAHs (BAA, BBF, BKF, BAP, DBAH and IND) according to the International Agency for Research on Cancer (IARC - [w_{16}]), it was observed that they represent 38% of total concentration for Estarreja samples. Therefore the contamination of PAHs in Estarreja represents a health hazard.

Table 7.9 - Median percentages of individual PAHs in Estarreja urban soils.

PAH	Median %	PAH	Median %
NP	0.7	**BAA**	5.5
ACY	1.2	**CRY**	9.2
ACE	1.1	**BBF**	11.4
FLU	0.5	**BKF**	6.5
PHE	6.5	**BAP**	6.5
ANT	1.7	**IND**	6.9
FLA	14.8	**DBAH**	1.8
PYR	12.9	**BGHI**	6.7

PCA was performed to investigate the spatial differences and similarities of PAHs patterns in soil samples from different sampling sites. Concentrations obtained from chemical analysis for the 16 compounds were log transformed and therefore the 16 eigenvalues extracted by PCA for log data are presented in Figure 7.7. Table 7.10 shows the factor loadings (with the ones higher than 0.5 marked in bold), eigenvalues and percent of variance for the first two factors with eigenvalues higher than unit which explain by themselves 85.5% of total variance. Projection of the variables in the first factorial plan is shown in Figure 7.8 and projection of the cases on the first factorial plan is shown in Figure 7.9.

The first factor is loaded by the all PAHs except NP and ACE, being the last explained by the second axes. By observing the projection of variables on the first factor plan it's possible to distinguish the association between the mid to high molecular weight PAHs. Another group can be defined as the low molecular weight PAHs (ACE, FLU, ANT and PHE). ACY and NP are the more volatile compounds, that had very low recoveries.

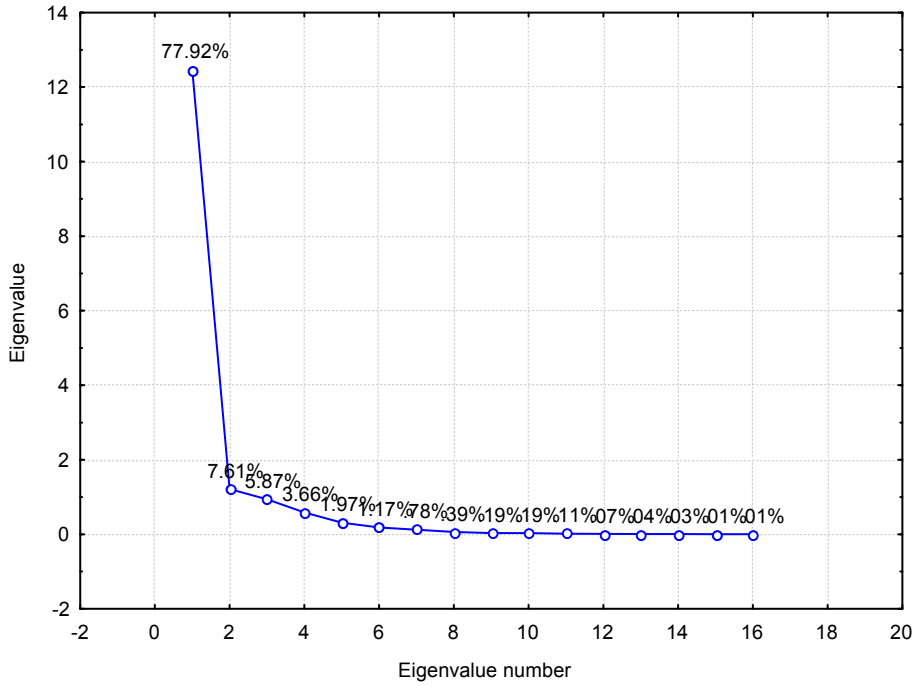


Figure 7.7 – Scree plot for the 16 eigenvalues.

Table 7.10 – Factor loadings, eigenvalues and percent of variance for the first two factors.

PAHs	Factor 1	Factor 2
NP	-0.259417	-0.491510
ACY	**-0.812647**	-0.290431
ACE	-0.360159	**0.684873**
FLU	**-0.716552**	**0.513571**
PHE	**-0.922805**	0.187379
ANT	**-0.858606**	0.254656
FLA	**-0.961280**	0.019619
PYR	**-0.968442**	-0.009753
BAA	**-0.963056**	-0.092471
CRY	**-0.980465**	-0.090521
BBF	**-0.985114**	-0.049260
BKF	**-0.983234**	-0.084582
BAP	**-0.974385**	-0.078305
IND	**-0.979992**	-0.091032
DBAH	**-0.979931**	-0.074451
BGHI	**-0.974649**	-0.106860
Eigenvalue	12.47	1.22
% Total	77.92	7.61
Cumulative	77.92	85.53

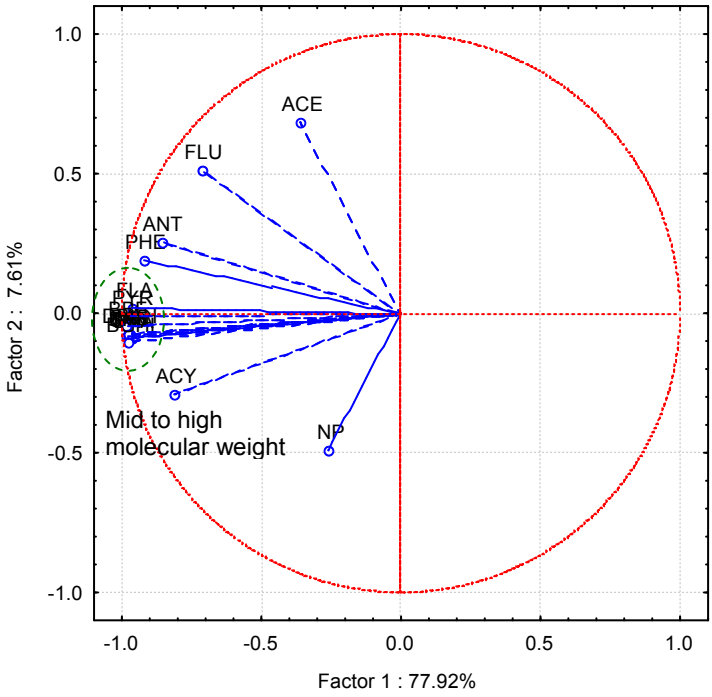


Figure 7.8 - Projection of the variables on the first factorial plane.

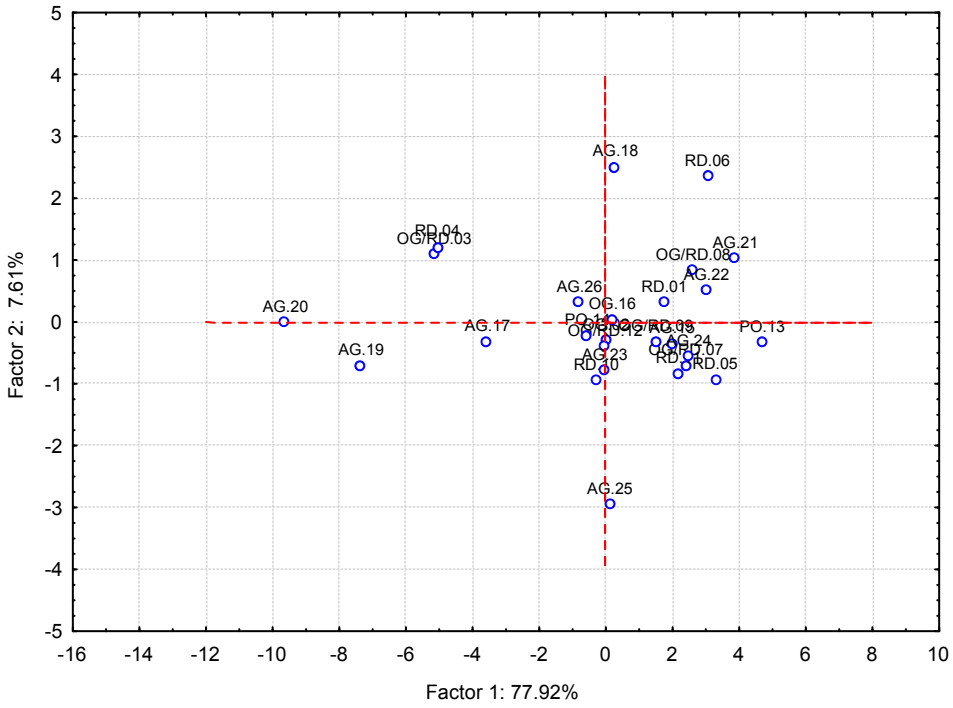


Figure 7.9 - Projection of the cases on the second factor plan.

Factor 1 (with an explained variance of 77.9%) condenses the information of the mid to high molecular PAHs as tracer of anthropogenic pollution (Table 7.10). Distribution of factor-scores for the first factor is given in Figure 7.10, indicating the relative strength of this factor in each sample. Figure 7.10 together with Figure 7.9 shows the samples likely to be affected by the presence of high molecular weight PAHs, being mainly agricultural samples (17, 19 and 20) located outside the urban area but close to each other. Figure 7.9 also shows the samples affected by lighter PAHs which are sample 3.OG/RD and 4.RD, located inside the urban area and close to the main road.

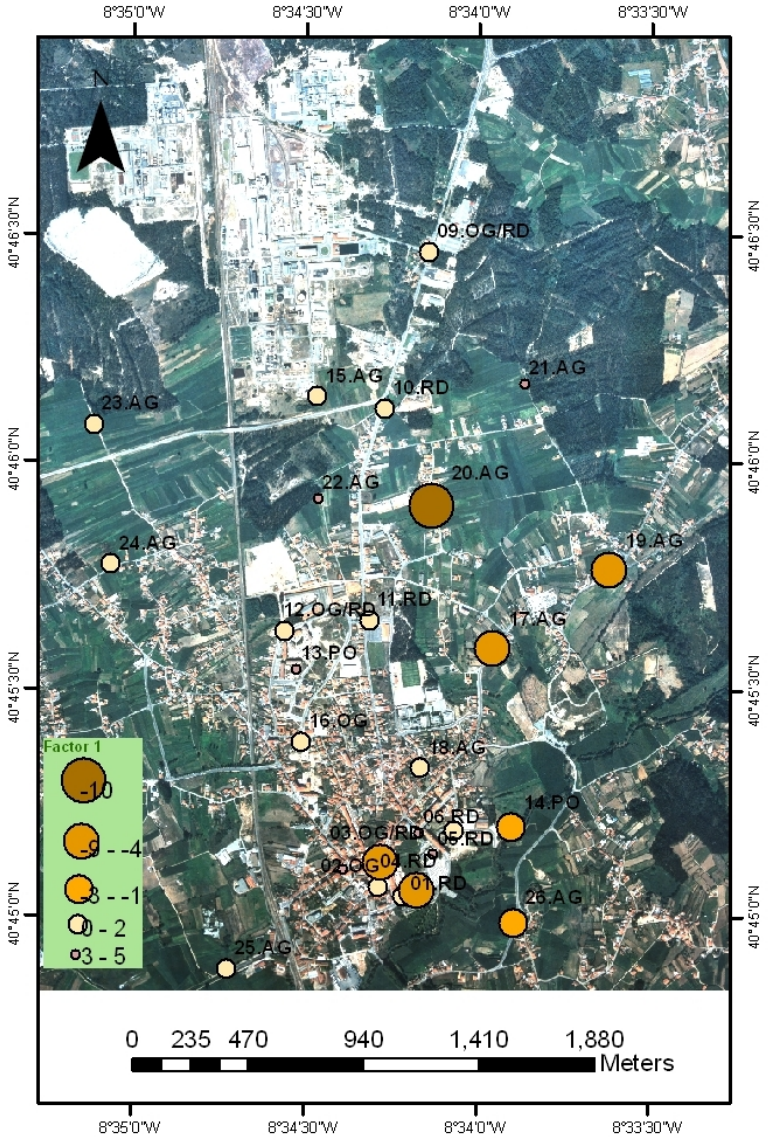


Figure 7.10 - Distribution of factor-scores for the first factor (ACY, FLU, PHE, ANT, FLA, PYR, BAA, CRY, BBF, BKF, BAP, IND, DBAH, BGHI).

7.3.3 Soil parameters affecting PAHs and PCBs distribution

In order to asses the influence of other soil parameters such as OM, C/N, texture, pH and PTM, principal component analysis was performed. The initial matrix, obtained after log transformation of data, was constituted by 26 individuals and 13 variables and the eigenvalues extracted by PCA are presented in Figure 7.11. Table 7.11 shows the factor loadings (with the ones higher than 0.5 marked in bold), eigenvalues and percent of variance for the first four factors with eigenvalues higher than unit which explain by themselves 57.5% of total variance.

Factor 1 is loaded by Pb, silt, Fe, Cu, Zn, OM and Hg in opposition to sand. The second factor is loaded by the SumPCBs and again by Hg in opposition to C/N. The third factor is loaded by the PCBs and PAHs in opposition to Cd and the fourth factor by pH. The third factorial plan is not represented as its contribution is not significant for the organic contaminants distribution.

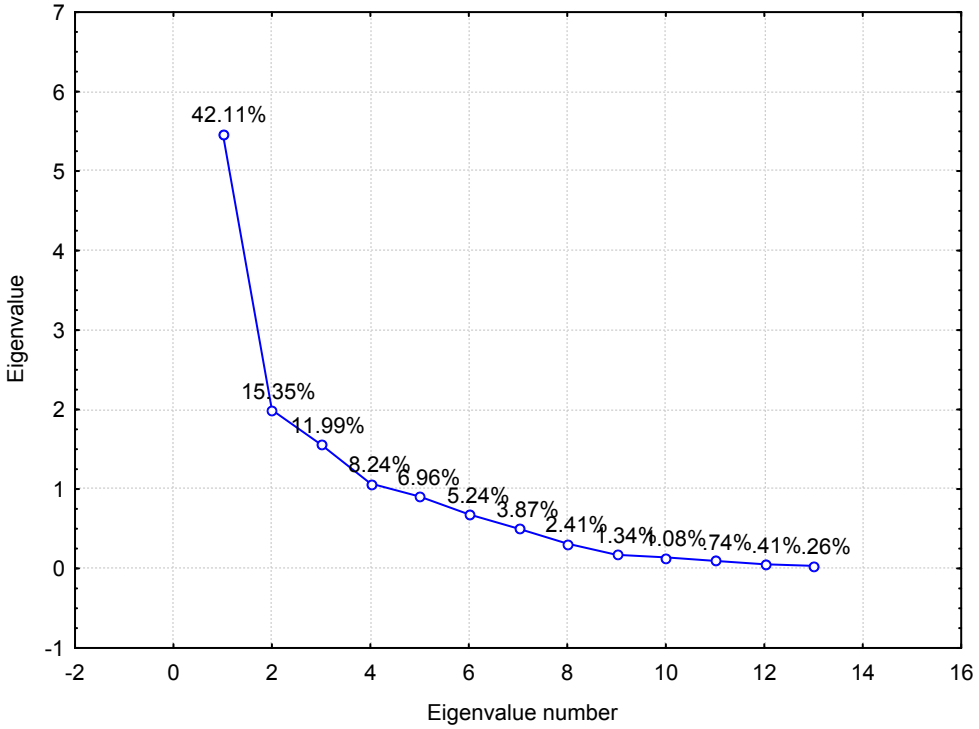


Figure 7.11 – Scree plot of the 13 eigenvalues obtained.

Table 7.11 – Factor loadings, eigenvalues and percent of variance for the first four factors.

	Factor 1	Factor 2	Factor 3	Factor 4
Cu	**-0.811779**	-0.054249	0.278243	0.249726
Pb	**-0.855003**	-0.223998	-0.219462	0.013461
Zn	**-0.797911**	-0.423425	0.187125	-0.015395
Fe	**-0.837638**	0.303841	0.303452	0.038805
Cd	-0.442875	-0.198530	**0.532835**	0.455740
Hg	**-0.588514**	**-0.603090**	0.044188	-0.232648
pHCa	0.226682	0.083303	0.474536	**-0.677100**
OM	**-0.737860**	0.444956	-0.318968	-0.265783
C/N	-0.126357	**0.643987**	-0.377471	0.351155
Silt	**-0.845428**	0.372529	-0.052024	-0.148080
SumPAHs	-0.224380	-0.309691	**-0.524940**	-0.177821
SumPCBs	-0.367283	**-0.518691**	**-0.519791**	0.059468
Sand	**0.831760**	-0.379917	-0.047597	0.189802
Eigenvalue	5.4744	1.9956	1.5587	1.0716
% Total	42.1	15.4	12.0	8.2
Cumulative	42.1	57.5	69.5	77.7

The factorial plan defined by the first two axes contains 57.5% of the total information of the correlation matrix, explaining 10 of the 13 variables (Figure 7.12). It's evident from Figure 7.12**,** the projection of variables on the first factorial plan, the presence of two groups separated by factor 2. The first one is formed by OM, silt and Fe and other by the PTMs together with sumPCBs. Therefore it's possible to conclude that second factor is more likely to be related with anthropogenic pollution, as Hg and Sum of PCBs are typical anthropogenic pollutants. Moreover from the previous chapter it is known that Hg, Zn and Pb are metals having influence in their distribution on Estarreja soils.

Although factor 1 is statistically dominant (with an explained variance of 44.5%), the factor 2 that explains only 12.4% but condenses the information of SumPCBs and Hg as tracer of pollution. Therefore the distribution of factor-scores for the second factor is shown (Figure 7.13), indicating the relative strength of this factor in each sample. Negative anomalies represents sites were SumPCBs and Hg are having more influence, and positive anomalies samples the ratio C/N is having more importance. From this plot it's possible to observe that contamination due to Hg and sumPCBs is more or less spread over the studied area. In Figure 7.14 it is possible to identify two groups of samples which are having different contribution of both factors, being one constituted by samples near the chemical complex (factor 2) and other by samples from the town centre (factor 1).

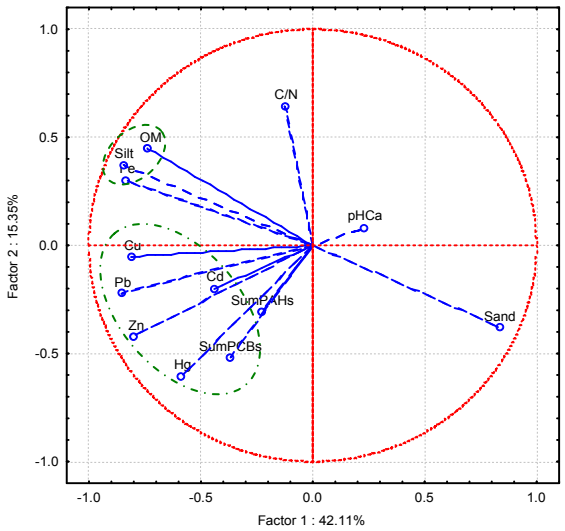


Figure 7.12 - Projection of the variables on the first factorial plane.

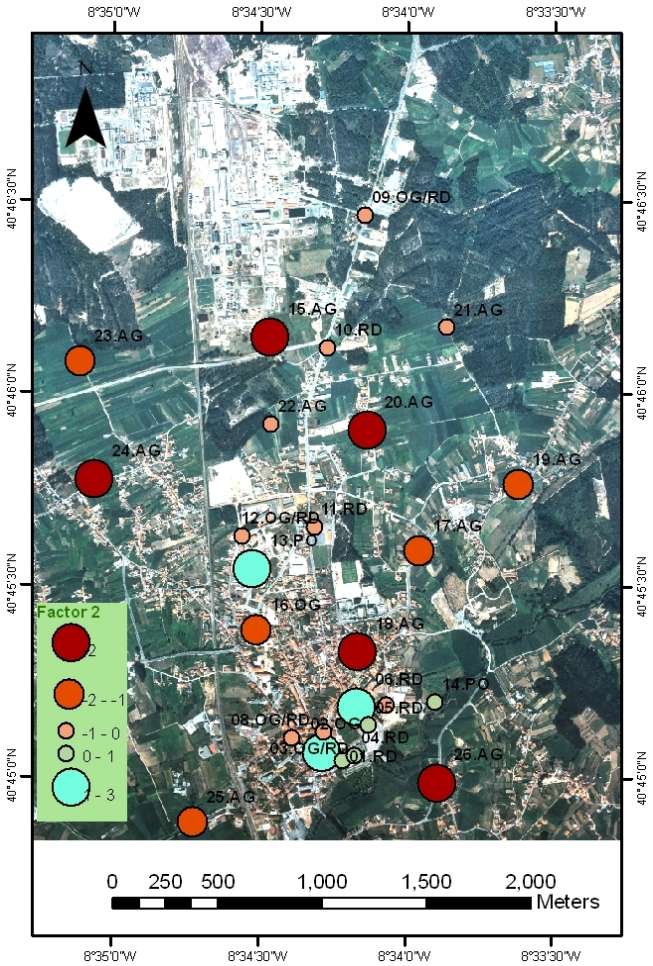


Figure 7.13 - Case contributions for the second factor (Hg, SumPCBs in opposition to C/N).

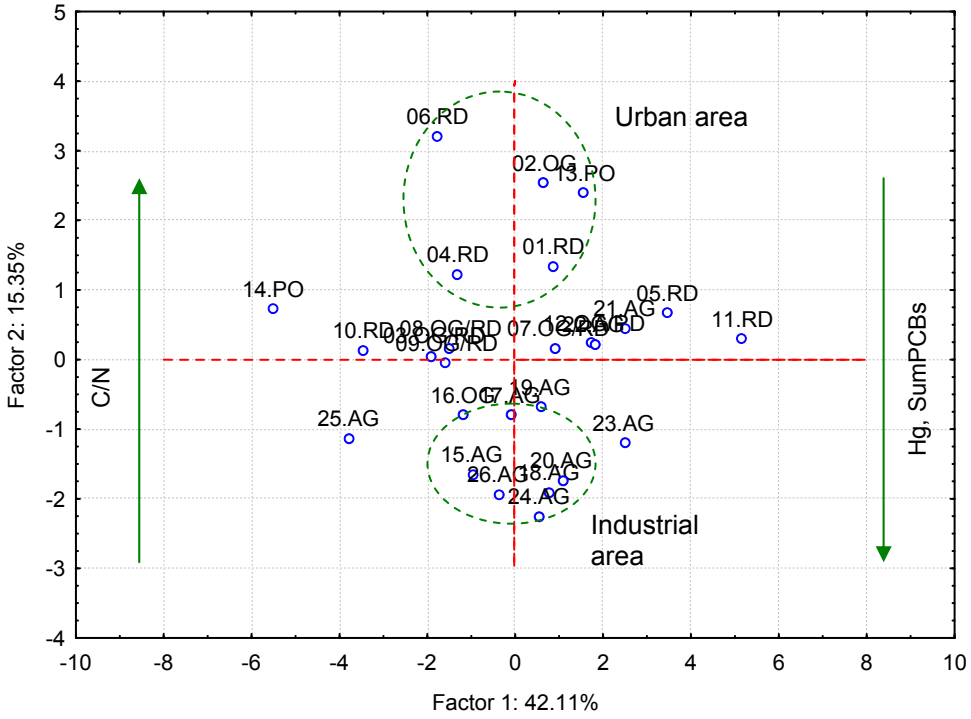


Figure 7.14 - Projection of the cases on the first factor plan.

The second factorial plan contains 54.1% of the total information of the correlation matrix, explaining 11 of the 13 variables (Figure 7.15). From this plan it's possible to observe the association between SumPCBs and PAHs in opposition to Cd. In what concerns factor 1, two groups can be distinguished separated by factor 2.

The third factor is responsible for 12% of explained variance however condenses the information of SumPCBs and SumPAHs as tracer of pollution. Therefore the distribution of factor-scores for the third factor is shown (Figure 7.16), indicating the relative strength of this factor in each sample. Negative anomalies represents sites were SumPCBs and SumPAHs are having more influence, and positive anomalies represents samples were Cd is having more importance. Both anomalies showed a similar distribution over the study area. In Figure 7.17 the influence of both factors in each sample can be observed.

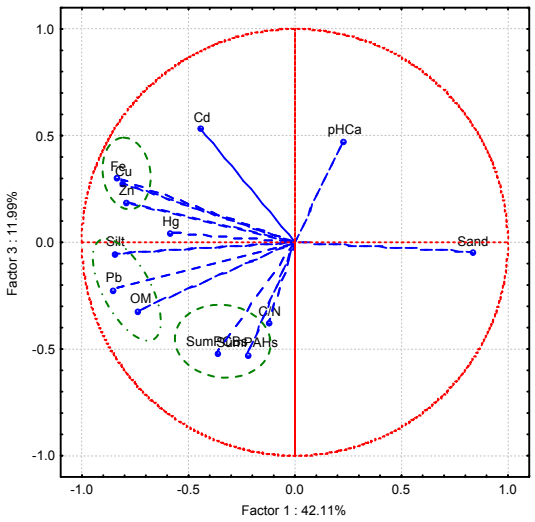


Figure 7.15 - Projection of the variables on the second factorial plane.

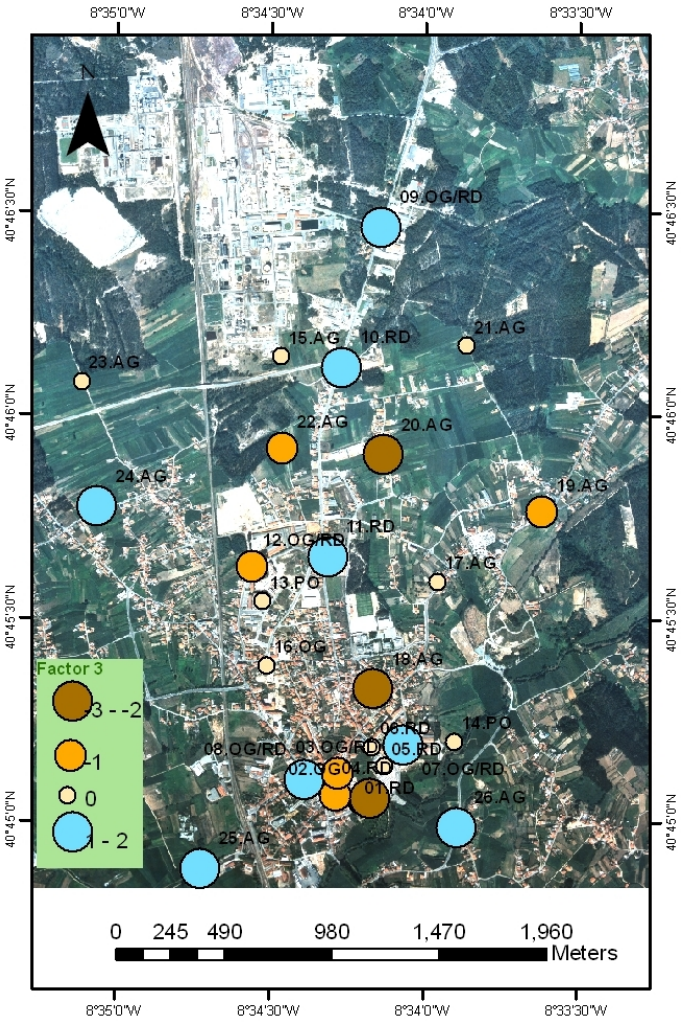


Figure 7.16 - Case contributions for the third factor (SumPCBs, SumPAHs in opposition to Cd).

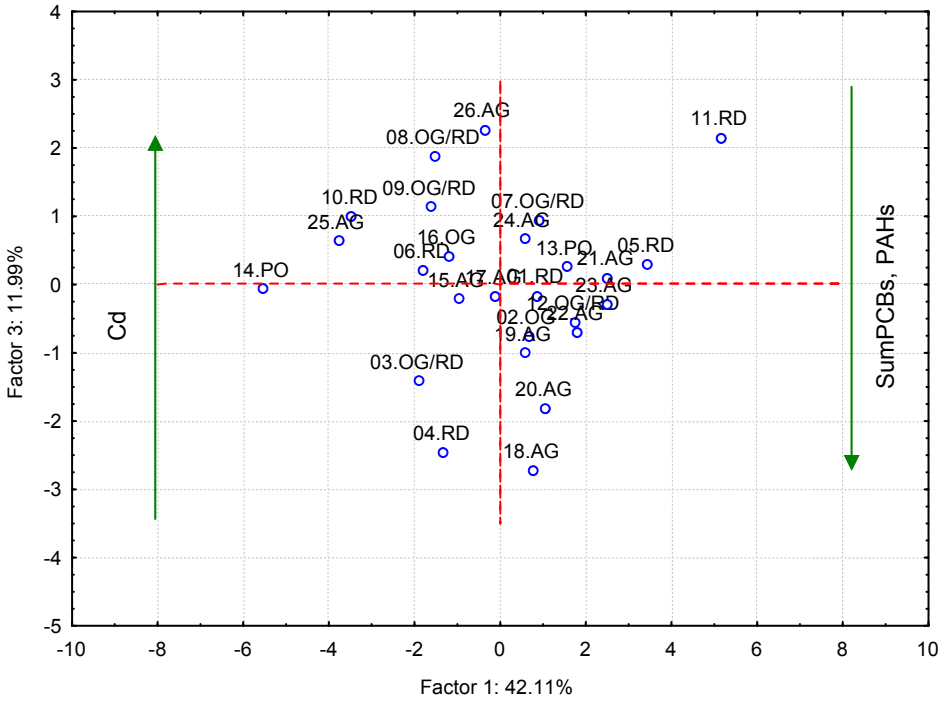


Figure 7.17 - Projection of the cases on the second factor plan.

From this PCA it was possible to conclude that the source of PCBs, as it was suspected, is the industry, as it was associated with other pollutants with this origin. Neither PCBs nor PAHs showed an evident influence of OM, pH or texture in their distribution as it was expected.

7.4. Conclusions

The spatial distribution of PCB concentrations seems homogeneous over the sampling area, indicating diffuse pollution from atmospheric deposition. However it should be noted that the most problematic samples are in accordance with the results of PTM (except sample 18). The PCBs levels were found to be low for an urban area, when compared with previous studies, being the pattern more similar to the one found in remote areas what can indicate long term pollution.

Concentration of PAHs in Estarreja soils is comparable with soils of other European cities. Two samples were considered heavily contaminated and other two weakly contaminated. Most abundant PAHs were FLA and PYR followed by BBF and CRY, being these PAHs usually associated with the combustion of fossil fuel and other burnable materials (confirmed by the signature revealed by the ratio of indicative PAHs). Samples

likely to be affected by the presence of high molecular weight PAHs, are mainly agricultural samples located outside the urban area but very close to each other. However, samples affected by lighter PAHs are located inside the urban area and close to the main road. Moreover, the contamination of PAHs in Estarreja represents a health hazard as almost 40% of the PAHs emited are considered carcinogenic.

Although the mixed signature of all the sources isn't clear to address with accuracy a source of PAHs (either industry or traffic), for PCBs it was more evident the influence of industry. Neither PCBs nor PAHs showed an evident influence of OM, pH or texture in their distribution as it was expected.

8. Conclusions

In order to conduct a survey on urban soils quality, first it is necessary to have a preliminary characterization of the ecosystem to better plan the sampling and to define the parameters to be analysed. This initial assessment includes the collection of background information about climate, hydrology, city history and also about the social organization, as socio-economic indicators are driving forces for the formation of a city as environment. Sampling is an essential step in urban soils quality assessment, and of complex planification since they are not considered as a continuous system, being repeatedly interrupted by roads, buildings foundations, pipes and cables. The set of indicators selected to assess urban soil quality will depend of the purpose of the study, city specifications and analytical capabilities of the laboratory. Moreover it is necessary to keep in mind that soil quality is a function of the intended use for the land.

Estarreja is a small city, well known for its chemical industry; activity whose importance has however been decreasing over the years. The area around the chemical complex and the lagoon (Ria de Aveiro) as been subject to several studies, but none was carried out in the urban area. In the last years population in the urban centre is increasing, therefore affecting the land consumption and anthropogenic pressures in soils, turning it important to have soil protection policies, especially in an area likely to be affected by industrial pollution.

Estarreja soils can be characterized as slightly acid, with low contents in organic matter and total carbon, and an organic matter enriched surface layer. The cation exchange capacity values are low, and the low nutrient status turn these soils very infertile. Some samples showed very high percentages of exchangeable Na, probably reflecting rainwater influence. In what regards texture, they are classified as sandy loam or loamy sand. Therefore, a high percentage of sand seems to be a natural feature of the studied area, except in the city centre, probably due to management practices of ornamental gardens. In spite of this, general parameters characterized were in accordance with the expected results due to soil type (podzols).

Concentrations of potentially toxic metals in Estarreja soils are, in general, not very high (comparing with other cities), with some sites showing values of Cu, Zn, Cd and Hg above the guidelines. Some hypothesis about the sources and pathways could be addressed from this study: Ni, Cd, Mn, Fe and Cr probably have a geogenic origin, while Pb, Cu, Zn, Cr, Hg have anthropogenic sources. Mercury is the most evident case

suggesting an anthropogenic origin, being this element also one of the most important contamination problems of the region.

PCBs concentrations are low for an urban area, when compared with other urban or industrialized areas. The spatial distribution of PCB concentrations seems homogeneous over the sampling area, indicating diffuse pollution from atmospheric deposition. It should be noted that some of the samples with higher concentrations are in agreement with metal concentrations. In addition, the profile of PCBs in Estarreja is dominated by hexa-chlorinated congeners which can be considered a tracer of long-term pollution.

Concentration of PAHs in Estarreja soils is comparable with soils of other European cities. PAHs pattern found is usually associated with the combustion of fossil fuel and other burnable materials. Samples likely to be affected by the presence of high molecular weight PAHs are mainly agricultural samples located outside the urban area but very close to each other. However, samples affected by lighter PAHs are located inside the urban area and close to the main road. Moreover, the contamination of PAHs in Estarreja represents a health hazard as almost 40% of the PAH emitted are considered carcinogenic.

Concerning the influence of land use on the indicators of soil quality, organic matter content is the parameter that seems to be more affected. In addition, Cu and Pb show higher concentrations in roadsides, even though not statistically proved. On the other hand, Zn, Hg, PAHs and PCBs show higher concentrations in agricultural sites, probably as a result of point source contamination. Moreover the point sources of potentially toxic metals identified were the Antuã river, the chemical complex and the Esteiro the Estarreja.

The parent material is a very important factor that will influence not only the natural concentrations of potentially toxic metals but also the soil properties itself. Moreover, general parameters characterization is in accordance with the expected results for this soil type and management practices. General properties of the soils, especially organic matter, show an influence on potentially toxic metals distribution. However, Hg and Cd are outliers in behaviour probably due to deposition from anthropogenic sources. In addition, organic contaminants distribution is not influenced by general soil parameters. An exception is the effect of the C/N ratio in SumPCBs distribution, that also showed an influence in the case of Hg.

Contributing to the control of the distribution/levels of potentially toxic metals (both those with recognized natural origin and the ones with anthropogenic origin), natural features of soils sampled (e.g., soil texture and especially organic matter content) results in some occurrences of low concentrations of most metals probably due to lixiviation of soils resulting in contaminations of the quaternary aquifer and streams.

This natural spatial variability of soils and the genesis of urban soils bring some difficulties regarding the assessment of the soils quality, being difficult to assess whereas contamination is due only to industry or if there is also a contribution of the urban area itself. In addition, the city size and the traffic density is expected to have a minor contribution to the pollution levels observed. Moreover all studied area seems to be affected by pollution. A larger set of sampling sites would allow a clear perception of the influence of the chemical complex: samples (with similar characteristics of texture and organic matter) collected at increasing distances from this source would more accurately highlight the importance of contamination arising from the chemical complex and the area of influence. A bigger set of sampling sites, with more samples of each land use type, would also enable to distinguish the real influence of each type of land use on soil quality. In the present study this influence was partially diluted by the specific characteristics of each sample.

In what concerns human health, the major threat is likely to be from agriculture and dust inhalation from the park near the river Antuã, with high levels of PTM, where children engage in ludic activities. Considering diet as a primary transfer pathway, it should be highlighted that the highest levels of persistent organic pollutants were found in agriculture sites, increasing the exposure risk through the ingestion of contaminated crops. This potential health hazard is relevant attending that it was found that in Estarreja, a significant fraction of PAHs are carcinogenic. Furthermore, the contamination observed in two agricultural sites in the east side of the study area should be further investigated in order to confirm the extent of the contamination and to determine its source.

Concluding, the set of indicators chosen can be used for a sustainable urban planning, allowing a more efficient management of resources available as well as an effective control of state changes occurring in the environmental quality of urban ecosystems. Moreover they allow to take some conclusions about the aptitude of a soil to the use, if soil is playing its role as a sink of contaminants and whereas it represents or not a hazard for human health.

9. References

Aamot, E., Steinnes, E., Schimid, R., 1996. Polycyclic aromatic hydrocarbons in Norwegian forest soils: impact of long range atmospheric transport. *Environmental Pollution* 92, 275-280.

Abreu, S.N., Pereira, M.E., Duarte, A.C., 1998. The use of a mathematical model to evaluate mercury accumulation in sediments and recovery time in a coastal lagoon (Ria de Aveiro, Portugal). *Water Science and Technology* 37 (6-7), 33-38.

AIDA (Associação Industrial do Distrito de Aveiro), 1994. Anuário Estatístico. Aveiro.

Alloway, B. J., 1995. The origin of heavy metals in soils. In: Heavy metals in soils. 2nd Ed. *Blackie Academic & Professional*, Glasgow, UK.

Azevedo, M. C. C., 1999. Contribuição para a caracterização ambiental da área envolvente do Complexo Químico de Estarreja. *Tese de Mestrado em Geoquimica. Departamento de Geociencias*, Universidade de Aveiro.

Baize, D., Sterckeman, T., 2001. Of the necessity of the knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. *The Science of Total Environment* 264, 127-139.

Barbizzi, S., de Zorgi, P., Belli, M., Pati, A., Sansone, U., Stellato, L., Barbina, M., Deluisa, A., Menegon, S., Coletti, V., 2004. Characterisation of a reference site for quantifying uncertainties related to soil sampling. *Environmental Pollution* 127, 131–135.

Barradas, J. M., 1992. Geoquímica de elementos maiores e vestigiais em amostras de solo, sedimentos de vala e águas subterrâneas. Contribuição para a caracterização ambiental da zona envolvente ao complexo de Estarreja. *Tese de Doutoramento. Departamento de Geociencias*, Universidade de Aveiro.

Barradas, J. M., Cardoso Fonseca, Ferreira da Silva, E. A., Garcia Pereira, H., 1992. Identification and mapping of pollution indices using a multivariate statistical methodology, Estarreja, central Portugal. *Applied Geochemistry* 7, 563-572.

Batista, A. C., Ferreira da Silva, E. A., Azevedo, M. C. C., Sousa, A. J., Cardoso Fonseca, E., 2002. Soil data analysis from central Portugal by Pricipal Component Analysis and geostatistical techniques. *Geochemistry: Exploration, Environment, Analysis* 2 (1), 15-25.

Bernaus, A., Gaona, X., van Ree, D., Valient, M., 2006. Determination of mercury in polluted soils surrounding a chlor-alkali plant. Direct speciation by X-ray absorption spectroscopy techniques and preliminary geochemical characterisation of the area. *Analytica Chimica Acta* 565, 73–80.

Biasioli, M, Barberis, R., Ajmone-Marsan, F., 2006. The influence of a large city on some soil properties and metals content. *Science of Total Environment* 356, 154-164.

Birke, M., Rauch, U., 2000. Urban geochemistry: invstigations in the Berlin metropolitan area. *Environmental Geochemistry and Health* 22, 233–248.

Bityukova, L., Shogenova, A., Birke, M., 2000. Urban geochemistry: a study of element distributions in the soils of Tallin (Estonia). *Environmental Geochemistry and Health* 22, 173-193.

Blanchard, M., Tei, M. J., Ollivon, D., Legenti, L., Chevreuil, M., 2004. Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France). *Environmental Research* 95, 184-197.

Boulding, J. R., 1994. Description and sampling of contaminated soils: a field guide. 2nd Ed. CRC Press. Florida, USA, 3.12 - 3.19, 3.65 - 3.77.

Carta Geológica de Portugal, 1972. Instituto Geográfico Português. Lisboa, Portugal.

CME (Câmara Municipal de Estarreja), 2003. Medidas preventivaS no âmbito do processo de revisão do Plano Director Municipal de Estarreja.

Coelho, J.P, Pereira, M.E., Duarte, A., Pardal, M.A., 2005. Macroalgae response to a mercury contamination gradient in a temperate coastal lagoon (Ria de Aveiro, Portugal). *Estuarine, Coastal and Shelf Science* 65 (3), 492-500.

Coelho, J.P, Rosa, M., Pereira, M.E., Duarte, A., Pardal, M.A., 2006. Pattern and annual rates of *Scrobicularia plana* mercury bioaccumulation in human induced mercury gradient (Ria de Aveir, Portuga). *Estuarine, Coastal and Shelf Science* 69, 629-635.

Condesso de Melo, M. T., Cabano, G. & Marques da Silva, M.A., 2002. Evolução hidrogeoquímica do Sistema Multiaquífero Quaternário de Aveiro. *Proceedings do 6º Congresso da Água*, Porto (Portugal), 18-22 Março. CD-Rom.

Condesso de Melo, M.T. 2002. Flow and hydrogeochemical mass transport model of the Aveiro Cretaceous multilayer aquifer (Portugal). *PhD Thesis. Departamento de Geociencias*, Universidade de Aveiro. Aveiro (Portugal).

Costa, C., Jesus-Rydin, C., 2001. Site investigation on heavy metals contaminated ground in Estarreja – Portugal. *Engineering Geology* 60, 39-47.

Covacia, A., Hurab, C., Schepensa, P., 2001. Selected persistent organochlorine pollutants in Romania. *The Science of the Total Environment*, 280, 143-152.

Craft, C. B., Seneca, E. D., Broome, S. W., 1991. Loss on ignition and Kjeldahl digestion for estimating organic carbon and total nitrogen in estuarine marsh soils: calibration with dry combustion. *Estuaries* 14 (2), 175-179.

Davidson, C.M., Urquhart, G.J., 2002. Soil Sampling Procedures, Project EVK4-CT-2001-00053: URBSOIL. Internal Report.

Diack, M., Stott, D. E., 2001. Development of a Soil Quality Index for the Chalmers Silty Clay Loam from the Midwest USA. Pages 550-555. In: Stott, D. E., Mohtar, R. H.,

Steinhart, G. C., 2001. The Global Farm. *10th International Soil Conservation Organization and Meeting*. May 24-29, 1999. USA

Doran, J.W., and Parkin, T.B., (1996) Quantitative indicators of soil quality: a minimum data set. In: Doran, J.W. and Jones, A.J. (Eds), Methods for assessing soil quality. *Soil Science Society of America*, Special Publication 49, Madison, W1, 25-37.

EC (European Commission), 2004. Working group on research, sealing and cross-cutting issues. *Task group 5 on soil sealing, soils in urban areas, land use and land use planning.* Final Report. Brussels, Belgium.

Edgar, P. J., Davies, I. M., Hursthouse, A. S., Matthews, J. E., 1999. The biogeochemistry of polychlorinated biphenyls (PCBs) in the Clyde: Distribution and Source Evaluation. *Marine Pollution Bulletin* 38(6), 486-496.

EEA (European Environmental Agency), 2005. EEA core set of indicators - Guide. EEA Technical Report No 1/2005. Luxembourg, 7.

Ellis, S., Mellor, A., 1995. Soils and environment. *Routledge,* 1st Ed, New York, USA, 45-52, 241-297.

Environment Canada, 2001, Tab #4 – Sampling & Analysis of Hydrocarbon Contaminated Soil, *Tabs on Contaminated Sites*, Ontario Region - Environmental Protection Branch.

Erickson M. D.,1997. Analytical chemistry of PCBs. Second Edition. *Lewis Publishers*, Boca Raton, New York.

Ferreira, M. M. S. I., 1993. Mercúrio em solos da área do complexo químico de Estarreja. *Tese de Mestrado em Geoquimica. Departamento de Geociencias*, Universidade de Aveiro.

Folch, I., Vaquero, M. T., Comellas, L., Broto-Puig, F., 1996. Extraction and clean-up methods for improvement of the chromatographic determination of polychlorinated biphenyls in sewage sludge-amended soils: elimination of lipids and sulphur. *Journal of Chromatography A* 719, 121-13.

Girvin D. C., Sklarem, D. S., Ainsworth, C. C., 1993. Polychlorinated Biphenyl sorption/desorption in soil-water systems, in Proceedings: 1993 PCB Seminar (New Orleans, LA: Electric Power Research Institute, Sept.14-17.

Guvenç, N., Alagha, O., Tuncel, G., 2003. Investigation of soil multi-element composition in Antalya, Turkey. *Environmental International* 29, 631-640.

Hall, A., 1982. Water qulity problems in Ria de Aveiro. In: Actual problems of oceanography in Portugal. *Ed. Junta Nacional de Investigação Científica e Tecnológica and Nato Marine Sciences Panel*, Lisboa, 159-169.

Huinink, J. Th. M., 1998. Soil quality requirements for use in urban environments. *Soil & Tillage Research* 47, 157-162.

Inácio, M. M., Pereira, V., Pinto, M. S., 1998. Mercury contamination in sandy soils surrounding an industrial emission source Estarreja, Portugal. *Geoderma* 85, 325–339.

INE, 2002. Recenseamento Geral da População e Habitação,*Censos 2001*. Lisboa.

ISO, 1994a. ISO Method 11464:1994. Soil quality - Pretreatment of samples for physico-chemical analyses.

ISO, 1994b. ISO Method 10390:1994 Soil quality -- Determination of pH.

ISO, 1995a. ISO Method 13536:1995. Soil quality -- Determination of the potential cation exchange capacity and exchangeable cations using barium chloride solution buffered at pH = 8.1.

ISO, 1995b. ISO 10694:1995. Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis).

IPCS, 1998. IPCS Environmental Health Criteria 2002. Selected Non Heterocyclic Polycyclic Aromatic Hydrocarbons. WHO, Geneva, 6-177.

ISS (Istituto Superiore di Sanita), 2003. Interpretaziona del parametro “PCB” – D.M. 471/99. Italia.

Jim, C. Y., 1998. Soil Characteristics and management in an urban park in Hong Kong. *Environmental Management* 22(5), 683-695.

Karlen, D. L., Mausbach, M. J., Doran. J. W., Cline, R. G., Harris, R. F., Schuman, G. E., 1997. Soil quality: A concept, definition, and framework for evaluation. *Soil Science Society of America Journal* 61 (1), 4-10.

Kelly, J., Thornton, I., 1996. Urban geochemistry: a study of the influence of anthropogenic activity on the heavy metal content of soils in traditional industrial and non-industrial areas of Britain. *Applied Geochemistry* 11, 363-370.

Koeleman, M., Willem, J., Ietswaart, H., 1999. Dispersion of PAHs and heavy metals along motorways in the Netherlands-an overview. *The Science of the Total Environment* 235, 347-349

Konen, M. E., Jacobs, P. M., Burras, C. L., Talaga, B. J., Mason, J. A., 2002. Equations for predicting soil organic carbon using loss-on-ignition for North Central U.S. soils. *Soil Science Society of America Journal* 66, 1878-1881.

Krauss, M., Wilcke, W., 2003. Polychlorinated naphthalenes in urban soils: analysis,concentrations, and relation to other persistent organic pollutants. *Environmental Pollution* 122, 75-89.

Kurfürst, U., Desaules, A., Rehnert, A., Muntau, H., 2004. Estimation of measurement uncertainty by the budget approach for heavy metal content in soils under different land use. *Accreditation and Quality Assurance* 9, 64-75.

Lead, W. A., Steinnes, E., Bacon, J. R., Jones, K. C., 1997. Polychlorinated biphenyls in UK and Norwegian soils: spatial and temporal trends. *The Science of the Total Environment* 193, 229-236.

Lindberg, S. E., 1998. Introduction: the Fourth International Conference on Mercury as a global pollutant. *Atmospheric Environment* 32(5), 807–808.

Machala, M., Vondrácek, J., Bláha, L., Ciganek, M., Neca, J., 2001. Hydrocarbon receptor-mediated activity of mutagenic polycyclic aromatic hydrocarbons determined using in vitro reporter gene assay. *Mutation Research* 497, 49–62.

Maliszewska-Kordybach, B., 1996. Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. *Applied Geochemistry* 11, 121-127.

Manta, D. S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M., 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy *The Science of Total Environment* 164, 125-133.

Marce, R. M., Borrull F., 2000. Solid-phase extraction of polycyclic aromatic compounds. *Journal of Chromatography A* 885, 273–290.

McMartin, I., Henderson, P. J., Plouffe, A., Knight, R. D., 2002. Comparison of Cu-Hg-Ni-Pb concentration in soils adjacent to anthropogenic point sources: examples from four Canadian sites. *Geochemistry: Exploration, Environment, Analysis* 2, 57-74.

Mielke, H. W., Wang, G., Gonzales, Le B., Quach, V. N., Mielke P. W., 2001. PAH and metal mixtures in New Orlean soils and sediments. *The Science of the Total Environment* 281, 217-227.

Mol, G., Vriend, S. P., van Gaans, P. F. M., 1998. Future trends, detectable by soil monitoring networks? *Journal of Geochemical Exploration* 62, 61-66.

Montelay-Massei, A., Ollivon, D., Garban, B., Teil, M. J., Blanchard, M., Chevreuil, M., 2004. Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere* 55, 555-565.

Monterroso, P., Pato, P., Pereira, E., Vale, C. a Duarte, A.C., 2003. Distribution and accumulation of metals (Cu, Cd, Zn and Pb) in sediments of a lagoon on the northwestern coast of Portugal. *Marine Pollution Bulletin* 46, 1200-1211.

Moreno, F., 2000. Estudo dos mecanismos de dispersão de elementos vestegiais em sedimentos de corrente e águas superficiais da bacia hidrografica do Antuã. Avaliação de riscos e classificação de vulnerabilidades. *Tese de Doutoramento. Departamento de Geociencias*, Universidade de Aveiro. Aveiro (Portugal).

NEPC (National Environment Protection Council), 1999. Guideline on laboratory analysis of potentially contaminated soils. *Schedulle B (3)*. Australia.

Norra, S., Stüben, D., 2003. Urban Soils. *Journal of Soils & Sediments* 3(4), 230-233.

Paterson, E., Sanka, M., Clark L., 1996. Urban soils as pollutant sinks - a case study from Aberdeen, Scotland. *Applied Geochemistry* 11, 129-131.

Paya-Perez A. B., Riaz, M., Larsen, B. R.,1991. Soil sorption of 20 PCB Congeners and six Chlorobenzenes. *Ecotoxicology and Environmental Safety* 21, 1-17.

Peltola, P., Åström, M., 2003. Urban Geochemistry: a multimedia and multielement survey of a small town in northern Europe. *Environmental Geochemistry and Health* 25, 397–419.

Pereira, M.E., Duarte, A.C., Millward, G.E., Abreu, S.N., Reis, M. C., 1997. Distribution of mercury and other heavy metals in the Ria the Aveiro. *Química Analitica* 16 (1), S31-S35.

Pereira, M.E., Duarte, A.C., Millward, G.E., Vale, C., Abreu, S.N., 1998. Tidal export of particulate mecury from the most contaminated area of Aveiro's Lagoon, Portugal. *The Science of Total Environment* 213, 157-163.

Pereira, E., Vale, C., Tavares, C. F., Válega, M., Duarte, A. C., 2005. Mercury in Plants from Fields Surrounding a Contaminated Channel of Ria de Aveiro, Portugal. *Soil & Sediment Contamination* 14, 571–577.

Portaria n.° 176/96, de 3 de Outubro (II Série). Ministérios da Agricultura, do Desenvolvimento Rural e das Pescas e do Ambiente.

Ramalhosa, E., Monterroso, P., Abreu, S., Pereira, E., Vale, C., Duarte, A., 2001. Storage and export of mercury from a contaminated bay (Ria de Aveiro, Portugal). *Wetlands Ecology and Management* 9, 311–316.

Reis, J., Tolda, J., Coelho, L. and Marinheiro, C., 1996. Potencialidades e factores de dinamização dos concelhos de Águeda e Estarreja. *Observatório do Emprego e Formação Profissional,* Lisboa.

Rodrigues, S., Pereira, E., Sarabando, L., Lopes, L., Cachada, A., Duarte, A., 2006. Spatial distribution of total Hg in urban soils from an Atlantic coastal city (Aveiro, Portugal). Science of Total Environment 368 (1), 40-46.

Rost, H., Loibner, P., Marion, H., Braun, R., Szolar, O. H. J., 2002. Behaviour of PAHs during cold storage of historically contaminated soil samples. *Chemosphere* 49, 1239-1246.

Russel, E. W., 1973. Soil conditions and plant growth. *10th Ed. Logman Group Limited*. London. 60-75, 89-128, 282-324, 604-628.

Schraps, W. G., Baumgarten, H., 2000. Investigation and large-scale mapping of soils in urban areas – Testsite Krefeld. 7th ConSoil,18-22 September, Leipzig, Germany.

SPAC (Soil and Plant Analysis Council, Inc), 1999. Soil analysis handbook of reference methods. Major cations (Potassium, calcium, magnesium and sodium). pp: 93-114. ; Organic and humic matter, pp: 175- 184. *Soils and Plant Analysis Council*. *CRC Press*. Athens, Ga.

Stevenson, F. J., 1982. Humus chemistry: genesis, composition, reactions. *John Wiley & Sons*, Inc. New York. 285-298; 404-409.

Schumacher, B. A., 2002. Methods for determination of total organic carbon (TOC) in soil and sediments. *Ecological Risk Assessment Support Centre*. USEPA.

Tan, K. H., 1994. Environmental soil science. *Marcel Dekker, Inc. New York*, 135-138, 241-246.

Tang, L., Tang, X.Y., Zhu, Y.G., Zheng, M.H., Miao, Q.L., 2005. Contamination of polycyclic aromatic hydrocarbons (PAHs) in urban soils in Beijing, China. *Environment International* 31, 822-828

Teixeira, C. & Zbyszewski, G., 1976. Carta Geológica de Portugal, Folha 13C, escala 1:50000, *Serv. Geol. de Portugal*, Lisboal.

Theocharopoulos, S. P., Wagner, G., Sprengart, J., Mohr, M-E., Desaules, A., Muntau, H., Christou, M., Quevauviller, P., 2001. European soil sampling guidelines for soil pollution studies. *The Science of Total Environment* 264, 51-62.

Trapido, M., 1999. Polycyclic aromatic hydrocarbons in Estonian soil: contamination and profiles. *Environmental Pollution* 105, 67-74.

UNEP, 1992. Decision guidance documents. Polychlorinated Biphenyls. *United Nations Environmental Programme*. Rome-Geneva.

University of Wageningen, 2000. Methodology of Chemical Soil and Plant Analysis. *Department of Soil Science and Plant Nutrition*. Netherlands (CM 06172309).

USEPA (United States Environmental Protection Agency), 1996a. Chapter Four – Organic Analytes. Revision 3. SW 846 *Test Methods for Evaluating Solid Wastes*, Revision 3.

USEPA (United States Environmental Protection Agency), 1996b. Method 8270C – Semivolatile organic compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Revision 3. SW 846 *Test Methods for Evaluating Solid Wastes*, Revision 3.

USEPA (United States Environmental Protection Agency), 2000. Method 3500B - Organic extraction and sample preparation. SW 846 *Test Methods for Evaluating Solid Wastes*, Revision 3.

Vangronsveld, J., Colpaert, J. V., Van Tichelen, K. K., 1996. Reclamation of bare industrial area contaminated by non-ferrous metals: physico-chemical and biological evaluation of the durability of soil treatement and revegetation. *Environmental Pollution* 94 (2), 131-140.

VROM, 2000. Circular on target values and intervention values for soil remediation: DBO/1999226863, Ministry of Housing, Spatial Planning and Environment Directorates-General for Environment Protection, Department of Soil Protection, *Netherlands Government Gazette*, No. 39.

Waite, S. 2000. Statistical ecology in practice: a guide to analysing environmental and ecological field data. 1st edition. *Prentice Hall*. Essex, England.

Wagner, G., Mohr, M-E., Sprengart, J., Desaules, A., Muntau, H., Theocharopoulos, S., Quevauviller, P., 2001. Objectives, concept and design of the CEEM soil project. *The Science of Total Environment* 264, 3-15.

Wagrowski, D. M., Hites, R. A., 1997. Polycyclic Aromatic Hydrocarbon Accumulation in Urban, Suburban, and Rural Vegetation. *Environmental Science and Technology* 31(1), 279-282.

Wang, G., Mielke, H.W., Quach, V., Gonzales, C., Zhang, Q., 2004. Determination of Polycyclic Aromatic Hydrocarbons and Trace Metals in New Orleans Soils and Sediments. *Soil & Sediment Contamination* 13, 313–327

Weiss, P., Lorbeer G., Scharf S., 2000. Regional aspects and statistical characterisation of the load with semivolatile organic compounds at remote Austrian forest sites. *Chemosphere* 40, 1159-1171.

Westman, C. J., Hytonen, J., Wall, A., 2006. Loss-on-ignition in the determination of pools of organic carbon in soils of forests and afforested arable fields. *Communications on Soil Science and Plant Analysis* 37, 1059:1075.

Wild, A., 1993. Soils and the environment: an introduction. *Cambridge University Press*. Cambridge. UK, 16-18, 32-36, 54-67, 130-136, 170-207.

Wilcke, W., Zech, W. Kobza, J., 1996. PAH-pools in soils along a PAH-deposition gradient. *Environmental Pollution* 92, 307–313.

Wilcke, W., Mueller, S., Kanchanakool, N., Niamskul, C., Zech, W., 1999. Polycyclic aromatic hydrocarbons in hydromorphic soils of the tropical metropolis Bangkok. *Geoderma* 91, 297-309.

Wong, F., Harner, T., Liu, Q.-T., Diamond, M. L., 2004. Using experimental and forest soils to investigate the uptake of polycyclic aromatic hydrocarbons (PAHs) along an urban-rural gradient. *Environmental Pollution* 129, 387-398.

Yang, Y., Ratté, D., Smets, B. F., Pinatello, J. J., Grasso, D., 2001. Mobilization of soil organic matter by complexing agents and implications for polycyclic aromatic hydrocarbon desorption. *Chemosphere* 43, 1013-1021.

Yong, R. N., Mohamed, A. M. O., Warkentin, B. P., 1992. Principles of contaminant transport in soils. *Elsevier*. Amsterdam 1st Edition.

Zhou, Q., Cabaniss, S. E., Maurice, P. A., 2000. Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Research* 34(14), 3505-3514.

Web references

[w_1] - ESRI: http://www.gis.com (2006)

[w_2] - Alfred Wegener Institute: http://www.awi-bremerhaven.de/GEO/Marine_GIS/Principles_GIS.htm#1 (2006)

[w_3] - Instituto Meteorológico: www.meteo.pt (2005)

[w_4] - INAG: www.inag.pt (2006)

[w_5] - CME: www.cm-estarreja.pt (2006)

[w_6] - AIDA: www.aida.pt (2006)

[w_7] - Quimigal: www.quimigal.pt (2006)

[w_8] - Uniteca: http://www.geocities.com/SoHo/Cafe/7398/uniteca.htm (2006)

[w_9] - Cires: http://www.cires.pt/ (2006)

[w_{10}] - Dow Portugal: http://www.dow.com/styrofoam/europe/pt/about/pabin01.htm (2006)

[w_{11}] - Instituto do Ambiente – Base de Dados On-line sobre a Qualidade do Ar: http://www.qualar.org/ (2006)

[w_{12}] - European Pollutant Emission Register: http://www.eper.cec.eu.int/eper (2007)

[w_{13}] - USDA (United States Department of Agriculture): http://ssldata.nrcs.usda.gov/ (2006)

[w_{14}] - CCME (Canadian Council of the Ministers of Environment): http://www.ccme.ca/assets/pdf/e1_06.pdf (2005)

[w_{15}] - http://sanaterre.com (2006)

[w_{16}] - IARC: http://www.iarc.fr/ (2005)

ANNEX I

Site Sampling Record

SITE SAMPLING RECORD

Name of Sampling Site			
Latitude/ Longitude			
Weather conditions		**Date/Time**	
Equipment used (e.g. auger etc)		**Sample container**	

Brief description of samples collected at each Sampling Point within each Sampling Site

Description	**Sample Ref.**	**Grid Ref.**

Diagram or precise description of sampling points

Name of sampler _____ **Signature** _____

ANNEX II

Location and description of Estarreja soils sampling sites

Data from site sampling records

Grid reference	Date	Weather conditions	X (Datum73)	Y (Datum73)	Relevant observations
EST.RD.01	03.05.05	Sun, hot	-36839.30	120389.58	Dark brown, some moisture; under grass, near a gas station
EST.OG.02	03.05.05	Sun, hot	-36938.58	120424.62	Dark brown, some moisture, under grass
EST.OG/RD.03	03.05.05	Sun, hot	-36932.74	120523.89	Brown, some moisture, under grass, old site
EST.RD.04	03.05.05	Sun, hot	-36785.83	120412.29	Brown, under grass, near a gas station
EST.RD.05	03.05.05	Sun, hot	-36716.47	120556.97	Brown, under grass
EST.RD.06	03.05.05	Sun, hot	-36771.78	120643.13	Brown, under grass, near a gas station
EST.OG/RD.07	03.05.05	Sun, hot	-36629.75	120656.26	Brown, under grass, round about
EST.OG/RD.08	03.05.05	Sun, hot	-37083.09	120496.90	Dark brown, under grass, round about
EST.OG/RD.09	03.05.05	Sun, hot	-36729.51	123011.12	Brown, under grass, old site
EST.RD.10	03.05.05	Sun, hot	-36910.75	122372.01	Brown, under grass
EST.RD.11	03.05.05	Sun, hot	-36974.92	121510.03	Very sandy soil with stones, under grass
EST.OG/RD.12	03.05.05	Sun, hot	-37323.53	121466.67	Brown, under grass, old site, round about
EST.PO.13	03.05.05	Sun, hot	-37273.23	121309.28	Brown, under grass, old site
EST.PO/RB.14	03.05.05	Sun, hot	-36397.38	120668.43	Dark brown, trees, near the river
EST.AG.15	03.05.05	Sun, hot	-37186.51	122422.30	Dark brown
EST.OG.16	04.05.05	Sun, hot	-37254.15	121017.47	Brown, under grass, tree line, old site, near a school
EST.AG.17	04.05.05	Sun, hot	-36474.91	121396.98	Brown, very hard
EST.AG.18	04.05.05	Sun, hot	-36768.62	120908.70	Dark brown, very hard, cultivated
EST.AG.19	04.05.05	Sun, hot	-35998.56	121715.94	Dark brown, cultivated
EST.AG.20	04.05.05	Sun, hot	-36723.18	121975.13	Brown, many roots, cultivated
EST.AG.21	04.05.05	Sun, hot	-36340.85	122470.00	Brown, , many roots, cultivated, fertilized
EST.AG.22	04.05.05	Sun, hot	-37181.65	122004.42	Brown, many roots, cultivated
EST.AG.23	04.05.05	Sun, hot	-38099.18	122310.44	Brown, cultivated
EST.AG.24	04.05.05	Sun, hot	-38028.26	121741.57	Brown
EST.AG.25	04.05.05	Sun, hot	-37558.05	120092.76	Brown, cultivated, fertilized
EST.AG.26	04.05.05	Sun, hot	-36389.30	120280.06	Brown, cultivated

ANNEX III

Results obtained for general indicators of urban soils quality

Table 1 - pH results

	H_2O		$CaCl_2$	
	SF	**SB**	**SF**	**SB**
01.RD	5.92	-	4.9	-
02.OG	6.15	6.14	5.34	4.96
03.OG/RD	6.60	6.08	5.83	4.90
04.RD	5.72	5.86	4.72	4.71
05.RD	6.45	6.54	5.5	5.94
06.RD	6.39	8.15	5.33	7.35
07.OG/RD	6.19	6.72	5.58	5.80
08.OG/RD	6.25	-	5.05	-
09.OG/RD	5.39	5.66	4.32	4.33
10.RD	5.64	6.18	4.92	5.20
11.RD	7.16	7.78	6.88	7.16
12.OG/RD	6.87	6.72	6.17	5.74
13.PO	6.37	6.53	5.47	5.56
14.PO	5.61	5.72	4.84	4.83
15.AG	6.39	4.53	5.24	4.03
16.OG	5.79	5.83	4.59	4.60
17.AG	5.75	5.57	4.58	4.48
18.AG	4.83	4.75	4.08	3.9
19.AG	6.38	6.21	5.82	5.03
20.AG	5.82	5.30	5.00	4.70
21.AG	6.23	6.09	4.78	4.64
22.AG	5.28	5.06	4.19	4.12
23.AG	6.29	7.19	5.3	6.52
24.AG	5.98	6.05	4.62	4.57
25.AG	6.82	5.59	6.07	4.92
26.AG	7.15	7.35	6.29	6.55

Table 2 – Particle size distribution results

Sample	% Sand Total	% Silt Total	% Clay Total	% fine fraction
01.RD	75.47	20.38	4.15	24.53
02.OG	57.92	34.89	7.19	42.08
03.OG/RD	60.22	35.45	4.32	39.78
04.RD	61.38	35.87	2.75	38.62
05.RD	78.43	16.27	5.30	21.57
06.RD	53.09	41.42	5.44	46.86
07.OG/RD	76.56	21.13	2.31	23.44
08.OG/RD	59.00	30.34	10.69	41.04
09.OG/RD	65.17	31.07	3.80	34.86
10.RD	55.45	40.86	3.64	44.50
11.RD	86.15	11.98	1.88	13.87
12.OG/RD	72.18	21.78	6.07	27.85
13.PO	64.30	28.90	6.81	35.70
14.PO	41.56	53.27	5.17	58.44
15.AG	77.68	18.58	3.74	22.32
16.OG	69.17	28.22	2.61	30.83
17.AG	74.75	21.39	3.88	25.27
18.AG	74.45	19.22	6.34	25.55
19.AG	71.53	22.78	5.71	28.49
20.AG	78.17	20.60	1.23	21.83
21.AG	73.55	21.57	4.88	26.45
22.AG	69.36	27.53	3.14	30.68
23.AG	75.55	20.32	4.13	24.45
24.AG	74.42	21.29	4.29	25.58
25.AG	52.67	37.52	9.81	47.33
26.AG	64.61	27.38	8.01	35.39

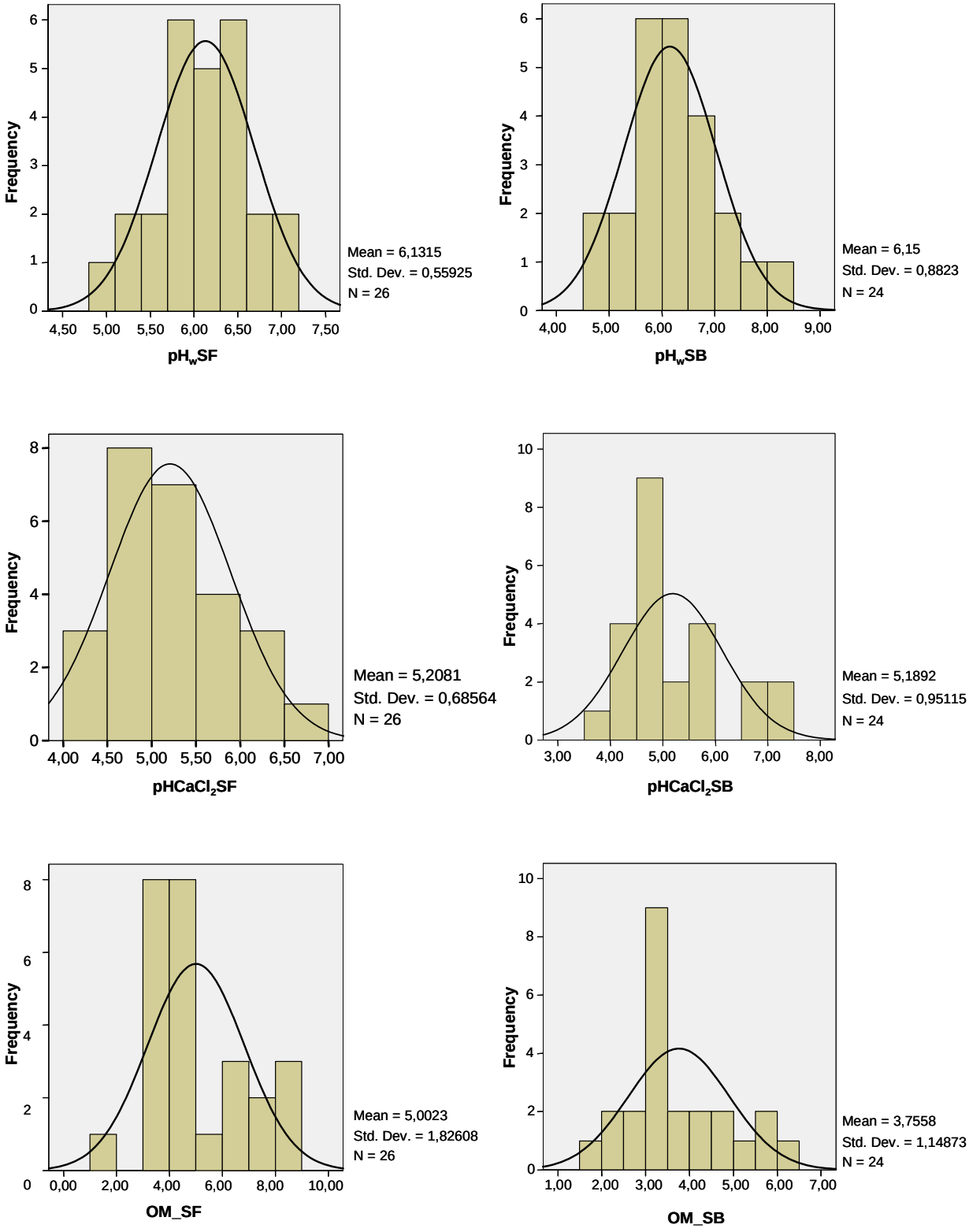


Figure 1 – Histograms of general characterization parameters

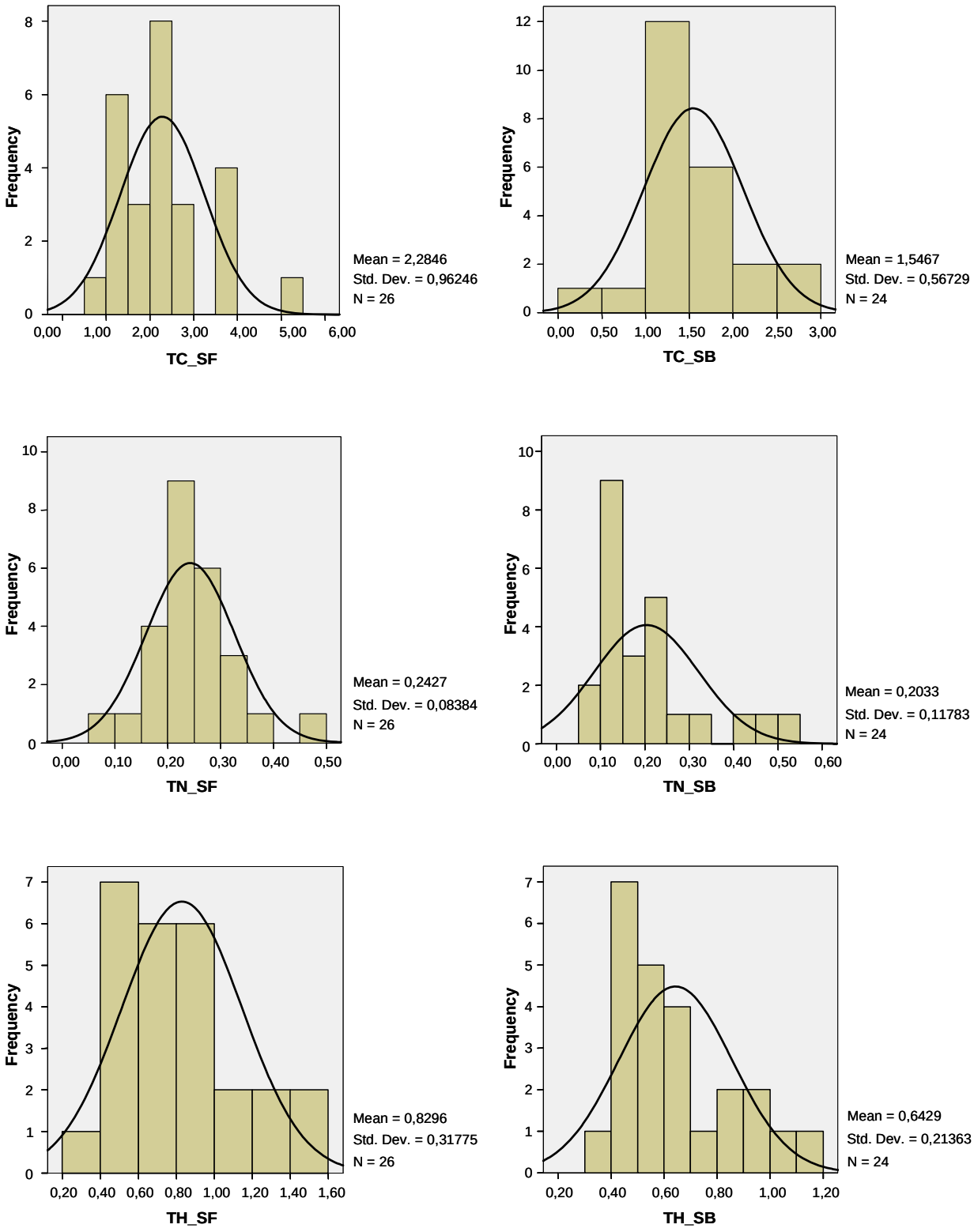
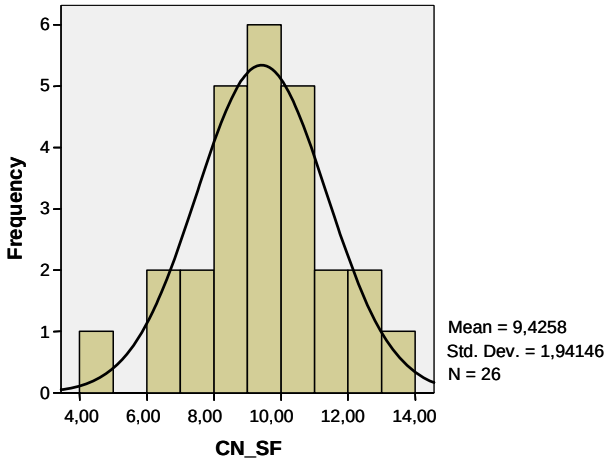
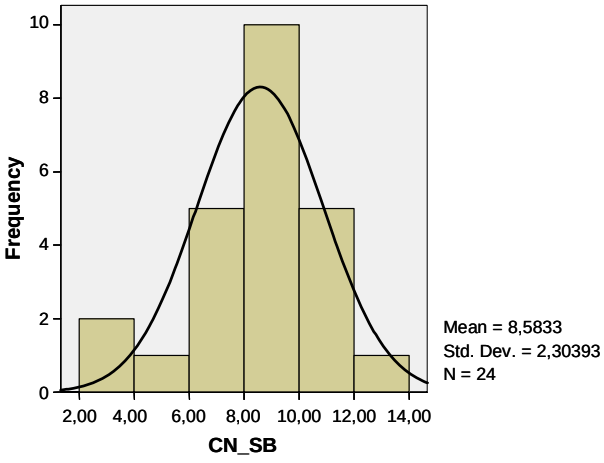
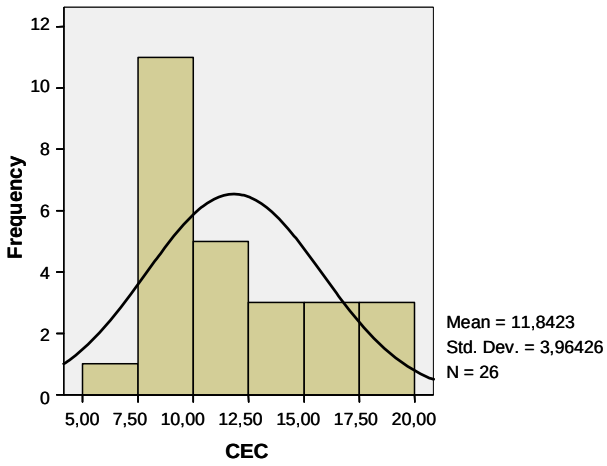
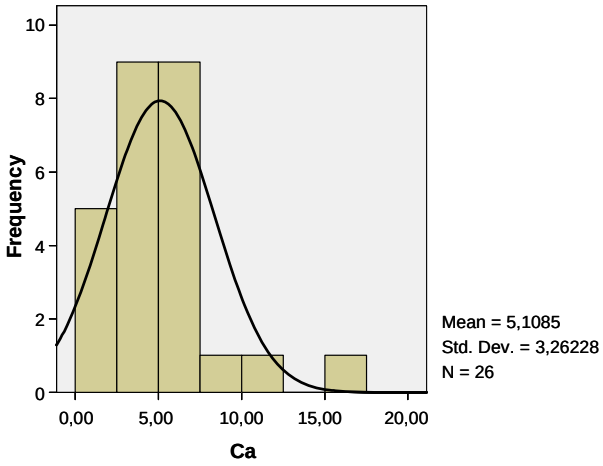


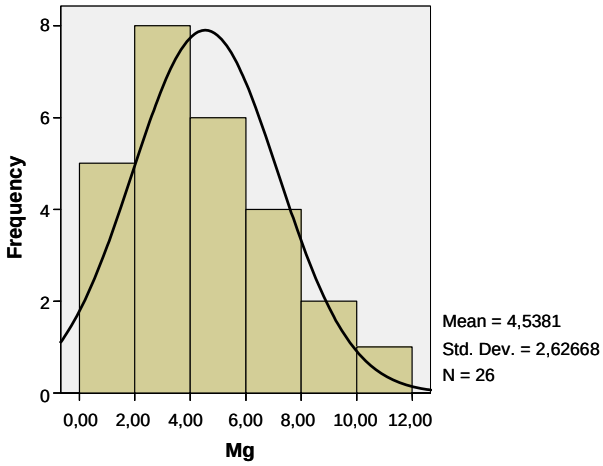
Figure 1 (cont.) – Histograms of general characterization parameters











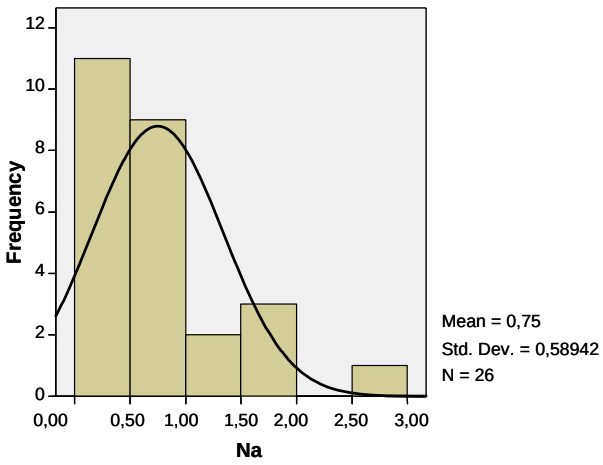


Figure 1 (cont.) – Histograms of general characterization parameters

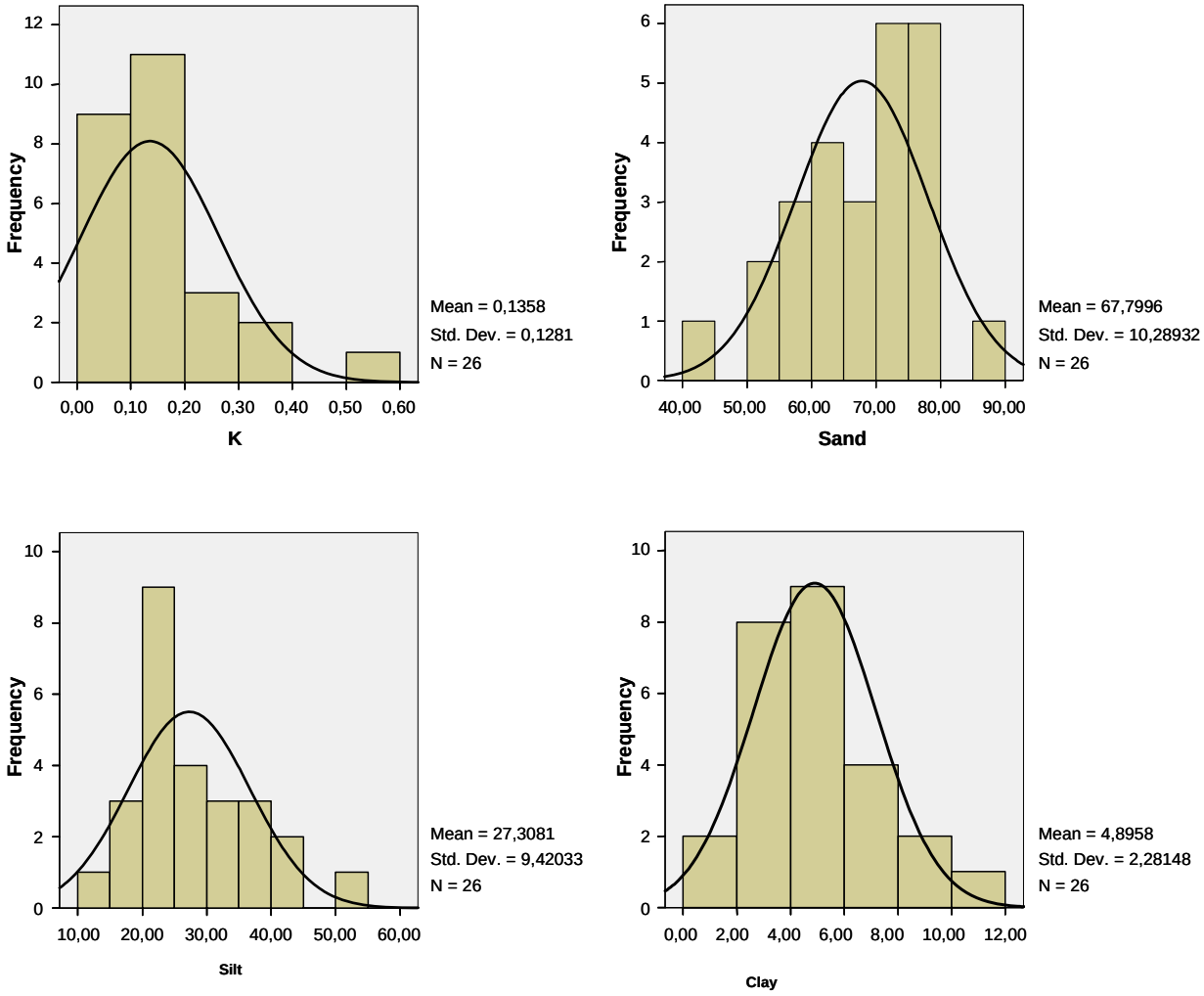


Figure 1 (cont.) – Histograms of general characterization parameters

Table 3 - Normality Test Kolmogorov-Smirnov, KS Distribution value, P value and the result for each sampling point

Parameter	Layer	K-S Dist	P	Normality Test
pH Water	SF	0.092	> 0.200	Passed
	SB	0.140	> 0.200	Passed
pH CaCl2	SF	0.091	> 0.200	Passed
	SB	0.191	0.023	Failed
OM	SF	0.196	0.012	Failed
	SB	0.198	0.016	Failed
TC	SF	0.186	0.021	Failed
	SB	0.198	0.016	Failed
TN	SF	0.196	0.011	Failed
	SB	0.220	0.004	Failed
TH	SF	0.115	> 0.200	Passed
	SB	0.149	0.178	Passed
C/N	SF	0.124	> 0.200	Passed
	SB	0.123	> 0.200	Passed
CEC	SF	0.166	0.063	Passed
Ca	SF	0.155	0.109	Passed
Na	SF	0.266	< 0.001	Failed
Mg	SF	0.122	> 0.200	Passed
K	SF	0.234	< 0.001	Failed
Ca	SF	0.155	0.109	Passed
Sand	SF	0.142	0.194	Passed
Silt	SF	0.185	0.023	Failed
Clay	SF	0.138	> 0.200	Passed
Fine fraction	SF	0.141	0.198	Passed

Table 4 - Pearson correlations

		$pHCaCl_2$	pHw	CEC	TC	TN	TH	CN	Sand
$pHCaCl_2$	Pearson Correlation	1	0.933**	0.039	0.035	0.187	0.041	-0.078	0.081
	Sig. (2-tailed)		0.000	0.851	0.864	0.360	0.841	0.705	0.695
pHw	Pearson Correlation	0.933**	1	0.052	0.001	0.191	0.001	-0.148	0.094
	Sig. (2-tailed)	0.000		0.802	0.996	0.349	0.998	0.471	0.646
CEC	Pearson Correlation	0.039	0.052	1	0.795**	0.696**	0.765**	0.421*	-0.819**
	Sig. (2-tailed)	0.851	0.802		0.000	0.000	0.000	0.032	0.000
TC	Pearson Correlation	0.035	0.001	0.795**	1	0.796**	0.788**	0.572**	-0.572**
	Sig. (2-tailed)	0.864	0.996	0.000		0.000	0.000	0.002	0.002
TN	Pearson Correlation	0.187	0.191	0.696**	0.796**	1	0.692**	-0.019	-0.564**
	Sig. (2-tailed)	0.360	0.349	0.000	0.000		0.000	0.928	0.003
TH	Pearson Correlation	0.041	0.001	0.765**	0.788**	0.692**	1	0.385	-0.811**
	Sig. (2-tailed)	0.841	0.998	0.000	0.000	0.000		0.052	0.000
CN	Pearson Correlation	-0.078	-0.148	0.421*	0.572**	-0.019	0.385	1	-0.184
	Sig. (2-tailed)	0.705	0.471	0.032	0.002	0.928	0.052		0.368
Sand	Pearson Correlation	0.081	0.094	-0.819**	-0.572**	-0.564**	-0.811**	-0.184	1
	Sig. (2-tailed)	0.695	0.646	0.000	0.002	0.003	0.000	0.368	
Silt	Pearson Correlation	-0.142	-0.175	0.798**	0.612**	0.542**	0.821**	0.263	-0.977**
	Sig. (2-tailed)	0.488	0.392	0.000	0.001	0.004	0.000	0.195	0.000
Clay	Pearson Correlation	0.222	0.297	0.394*	0.053	0.303	0.268	-0.256	-0.473*
	Sig. (2-tailed)	0.276	0.140	0.046	0.798	0.133	0.186	0.207	0.015
Fine Fraction	Pearson Correlation	-0.081	-0.095	0.818**	0.572**	0.564**	0.811**	0.184	-1.000
	Sig. (2-tailed)	0.695	0.646	0.000	0.002	0.003	0.000	0.369	0.000
Ca	Pearson Correlation	0.591**	0.551**	0.585**	0.567**	0.789**	0.516**	-0.012	-0.386
	Sig. (2-tailed)	0.001	0.004	0.002	0.003	0.000	0.007	0.952	0.052
Mg	Pearson Correlation	0.540**	0.460*	0.485*	0.573**	0.773**	0.583**	-0.018	-0.373
	Sig. (2-tailed)	0.004	0.018	0.012	0.002	0.000	0.002	0.929	0.061
Na	Pearson Correlation	-0.282	-0.398*	-0.176	-0.212	-0.174	-0.014	-0.120	-0.072
	Sig. (2-tailed)	0.163	0.044	0.390	0.299	0.396	0.947	0.559	0.725
K	Pearson Correlation	0.423*	0.399*	-0.099	-0.070	0.266	0.052	-0.441*	0.090
	Sig. (2-tailed)	0.031	0.044	0.632	0.734	0.189	0.800	0.024	0.663
OM	Pearson Correlation	-0.043	-0.060	0.923**	0.862**	0.724**	0.844**	0.480*	-0.809**
	Sig. (2-tailed)	0.833	0.772	0.000	0.000	0.000	0.000	0.013	0.000

**. Correlation is significant at the 0.01 level (2-tailed)

*. Correlation is significant at the 0.05 level (2-tailed)

Table 4 (cont.)- Pearson correlations

		Silt	Clay	Fine Fraction	Ca	Mg	Na	K	OM
$pHCaCl_2$	Pearson Correlation	-0.142	0.222	-0.081	0.591**	0.540**	-0.282	0.423*	-0.043
	Sig. (2-tailed)	0.488	0.276	0.695	0.001	0.004	0.163	0.031	0.833
pHw	Pearson Correlation	-0.175	0.297	-0.095	0.551**	0.460*	-0.398**	0.399*	-0.060
	Sig. (2-tailed)	0.392	0.140	0.646	0.004	0.018	0.044	0.044	0.772
CEC	Pearson Correlation	0.798**	0.394*	0.818**	0.585**	0.485*	-0.176	-0.099	0.923**
	Sig. (2-tailed)	0.000	0.046	0.000	0.002	0.012	0.390	0.632	0.000
TC	Pearson Correlation	0.612**	0.053	0.572**	0.567**	0.573**	-0.212	-0.070	0.862**
	Sig. (2-tailed)	0.001	0.798	0.002	0.003	0.002	0.299	0.734	0.000
TN	Pearson Correlation	0.542**	0.303	0.564**	0.789**	0.773**	-0.174	0.266	0.724**
	Sig. (2-tailed)	0.004	0.133	0.003	0.000	0.000	0.396	0.189	0.000
TH	Pearson Correlation	0.821**	0.268	0.811**	0.516**	0.583**	-0.014	0.052	0.844**
	Sig. (2-tailed)	0.000	0.186	0.000	0.007	0.002	0.947	0.800	0.000
CN	Pearson Correlation	0.263	-0.256	0.184	-0.012	-0.018	-0.120	-0.441*	0.480*
	Sig. (2-tailed)	0.195	0.207	0.369	0.952	0.929	0.559	0.024	0.013
Sand	Pearson Correlation	-0.977**	-0.473	-1.000	-0.386	-0.373	-0.072	0.090	-0.809**
	Sig. (2-tailed)	0.000	0.015	0.000	0.052	0.061	0.725	0.663	0.000
Silt	Pearson Correlation	1	0.274	0.977**	0.307	0.332	0.093	-0.134	0.830**
	Sig. (2-tailed)		0.175	0.000	0.127	0.097	0.652	0.515	0.000
Clay	Pearson Correlation	0.274	1	0.473*	0.469*	0.307	-0.056	0.148	0.216
	Sig. (2-tailed)	0.175		0.015	0.016	0.127	0.784	0.471	0.289
Fine Fraction	Pearson Correlation	0.977**	0.473*	1	0.386	0.372	0.072	-0.090	0.808**
	Sig. (2-tailed)	0.000	0.015		0.052	0.061	0.726	0.663	0.000
Ca	Pearson Correlation	0.307	0.469*	0.386	1	0.842**	-0.144	0.290	0.572**
	Sig. (2-tailed)	0.127	0.016	0.052		0.000	0.483	0.151	0.002
Mg	Pearson Correlation	0.332	0.307	0.372	0.842**	1	-0.172	0.423*	0.498**
	Sig. (2-tailed)	0.097	0.127	0.061	0.000		0.400	0.031	0.010
Na	Pearson Correlation	0.093	-0.056	0.072	-0.144	-0.172	1	-0.088	-0.107
	Sig. (2-tailed)	0.652	0.784	0.726	0.483	0.400		0.667	0.603
K	Pearson Correlation	-0.134	0.148	-0.090	0.290	0.423*	-0.088	1	-0.192
	Sig. (2-tailed)	0.515	0.471	0.663	0.151	0.031	0.667		0.346
OM	Pearson Correlation	0.830**	0.216	0.808**	0.572**	0.498**	-0.107	-0.192	1
	Sig. (2-tailed)	0.000	0.289	0.000	0.002	0.010	0.603	0.346	

**. Correlation is significant at the 0.01 level (2-tailed)

*. Correlation is significant at the 0.05 level (2-tailed)

ANNEX IV

Results obtained for potentially toxic metals in urban soils from Estarreja

Table 1 –Concentration of metals (mg/kg)

Sample	CATEGORY	CuSF	CuSB	PbSF	PbSB	ZnSF	ZnSB	MnSF	MnSB	FeSF (%)	FeSB (%)	NiSF	NiSB	CrSF	CrSB	CdSF	CdSB	HgSF	HgSB
1	RD.01	39.0	-	38.6	-	50.7	-	112	-	0.92	-	10.3	-	7.98	-	bdl	-	0.13	-
2	OG.02	13.4	14.7	21.9	26.3	35.7	34.9	147	174	1.15	1.34	9.42	9.85	12.0	13.3	bdl	bdl	0.05	0.06
3	OG/RD.03	41.2	41.2	64.0	78.1	106	69.9	239	241	1.03	1.15	7.71	9.85	10.6	10.6	0.20	0.31	0.20	0.20
4	RD.04	26.2	28.1	58.8	64.0	53.7	39.2	94.3	90.8	1.13	1.09	8.56	6.85	26.6	14.6	bdl	bdl	0.19	0.18
5	RD.05	8.94	11.5	17.5	21.9	33.6	34.1	105	117	0.68	0.76	6.85	4.71	12.0	9.31	bdl	0.25	0.07	0.07
6	RD.06	111	24.9	26.3	26.3	40.6	26.1	145	63.8	2.88	0.91	8.13	3.85	23.9	13.3	bdl	0.76	0.10	0.07
7	OG/RD.07	25.5	19.5	23.7	36.8	79.5	45.7	151	115	1.20	0.88	10.7	7.60	17.3	9.31	1.17	1.22	0.07	0.09
8	OG/RD.08	63.2	-	39.5	-	119	-	239	-	1.93	-	13.7	-	22.6	-	1.32	-	0.20	-
9	OG/RD.09	84.9	85.9	40.4	40.4	130	132	201	211	1.87	1.96	14.1	14.6	22.6	22.6	1.27	1.12	0.20	0.32
10	RD.10	111	50.1	52.6	41.2	194	123	221	223	2.04	1.96	16.3	16.7	30.6	21.3	1.73	1.43	0.45	0.26
11	RD.11	18.5	27.1	12.3	13.2	20.6	15.4	29.3	24.6	0.40	0.54	3.42	4.28	5.32	5.32	0.61	0.61	0.05	0.05
12	OG/RD.12	13.1	15.3	31.6	34.2	31.1	35.2	147	188	0.92	1.18	5.14	7.71	22.6	22.6	bdl	bdl 3	0.13	0.14
13	PO.13	19.8	22.7	18.4	22.8	28.8	28.7	151	186	1.01	1.17	11.1	9.42	17.3	20.0	bdl	bdl	0.05	0.05
14	PO.14	98.0	107	65.8	51.8	284	164	295	217	2.87	1.89	23.1	16.7	54.5	45.2	1.32	bdl	0.61	0.57
15	AG.15	73.4	20.1	49.1	33.3	256	59.8	139	53.2	0.88	0.59	8.13	7.92	20.0	14.6	0.20	bdl	1.47	0.76
16	OG.16	69.9	27.1	37.7	27.2	63.4	51.9	252	205	1.67	1.06	13.7	8.35	27.9	21.3	1.22	bdl	0.33	0.12
17	AG.17	69.6	76.0	36.0	37.7	55.2	52.4	276	284	1.05	1.11	9.85	8.99	12.0	12.0	0.66	bdl	0.18	0.23
18	AG.18	23.6	23.6	44.7	44.7	45.0	44.4	127	132	0.64	0.62	5.99	5.57	7.98	8.64	bdl	0.31	0.23	0.25
19	AG.19	20.8	28.4	25.4	23.7	78.4	41.8	115	99.2	0.85	0.98	8.13	8.56	9.97	10.6	0.31	0.25	0.17	0.09
20	AG.20	22.0	22.0	23.7	21.9	68.9	49.6	82.9	67.7	0.47	0.45	7.71	2.14	6.65	5.32	0.41	0.41	0.20	0.18
21	AG.21	9.26	9.58	19.3	20.2	30.0	28.7	84.7	84.7	0.53	0.54	2.14	2.57	7.31	7.98	0.46	0.51	0.12	0.12
22	AG.22	11.5	11.2	29.0	28.1	34.3	34.3	61.6	55.2	0.48	0.50	8.35	5.99	6.65	6.65	bdl	bdl	0.21	0.20
23	AG.23	14.7	15.0	18.4	19.3	51.3	50.1	61.4	60.6	0.45	0.45	6.42	5.57	5.32	6.65	bdl	bdl	0.21	0.23
24	AG.24	30.7	32.6	34.2	38.6	122	129	84.7	80.8	0.66	0.68	7.28	10.1	9.31	7.98	bdl	0.31	2.04	2.21
25	AG.25	54.3	40.2	64.0	51.8	169	108	209	196	1.84	1.56	16.7	12.8	27.9	21.3	0.61	0.41	4.53	2.99
26	AG.26	41.2	49.2	35.1	37.7	124	157	180	201	1.61	1.90	17.1	16.3	20.0	23.9	0.46	0.61	0.31	0.18

bdl = below detection limit

Table 2 - Normality Test Kolmogorov-Smirnov, KS Distribution value, P value and the result for each sampling point

Element	K-S Dist.	P	Normality Test
CuSF:	0.198	0.010	Failed
CuSB:	0.247	< 0.001	Failed
ZnSF:	0.206	0.006	Failed
ZnSB:	0.276	< 0.001	Failed
PbSF:	0.114	> 0.200	Passed
PbSB:	0.136	> 0.200	Passed
NiSF:	0.159	0.090	Passed
NiSB:	0.159	0.117	Passed
CrSF:	0.182	0.027	Failed
CrSB:	0.173	0.062	Passed
CdSF:	0.210	0.075	Passed
CdSB:	0.189	0.154	Passed
HgSF	0.371	< 0.001	Failed
HgSB	0.379	< 0.001	Failed
MnSF:	0.157	0.099	Passed
MnSB:	0.151	0.166	Passed
FeSF:	0.192	0.014	Failed
FeSB:	0.147	0.192	Passed

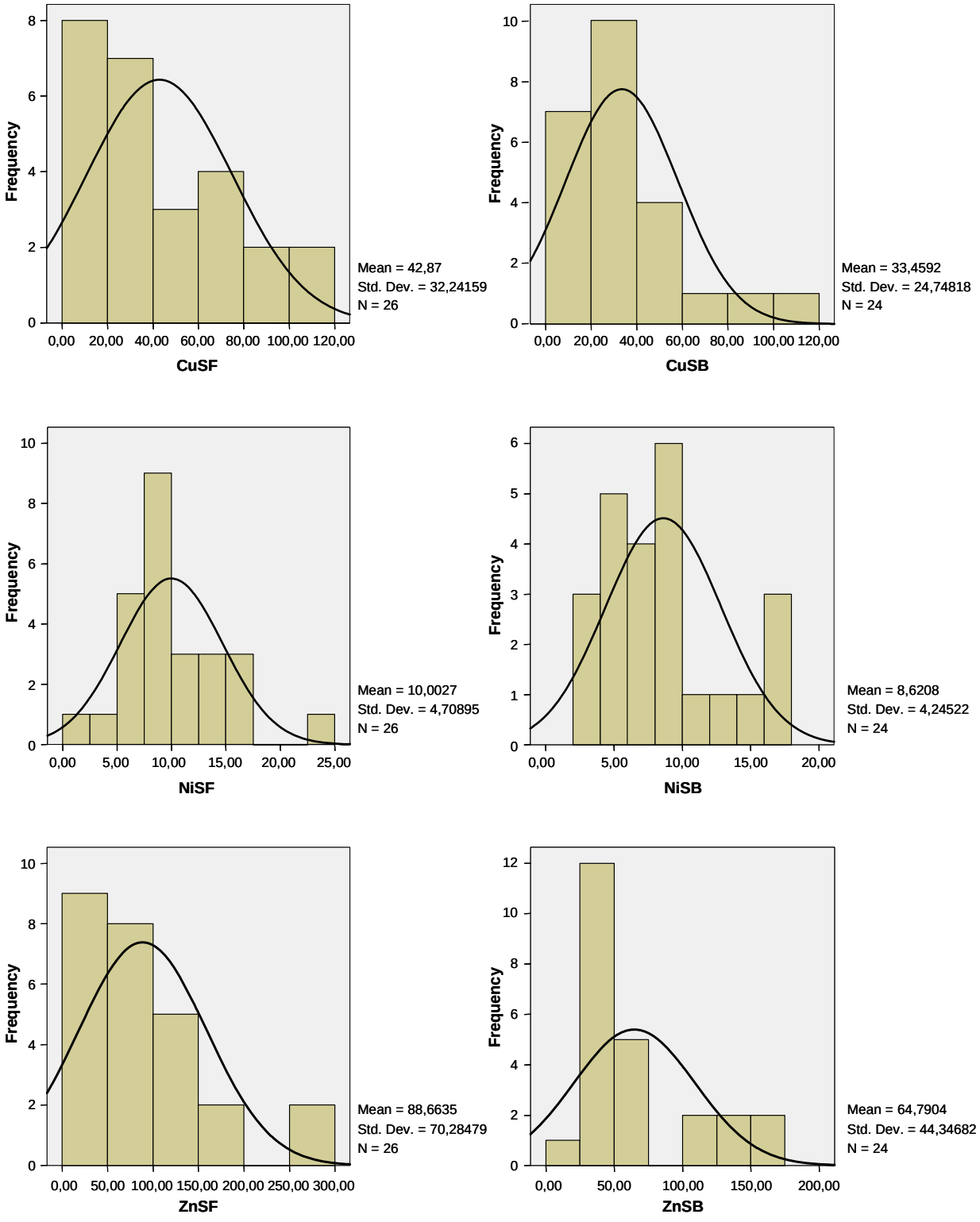


Figure 1 – Histograms of Cu, Ni and Zn for both SF and SB layer

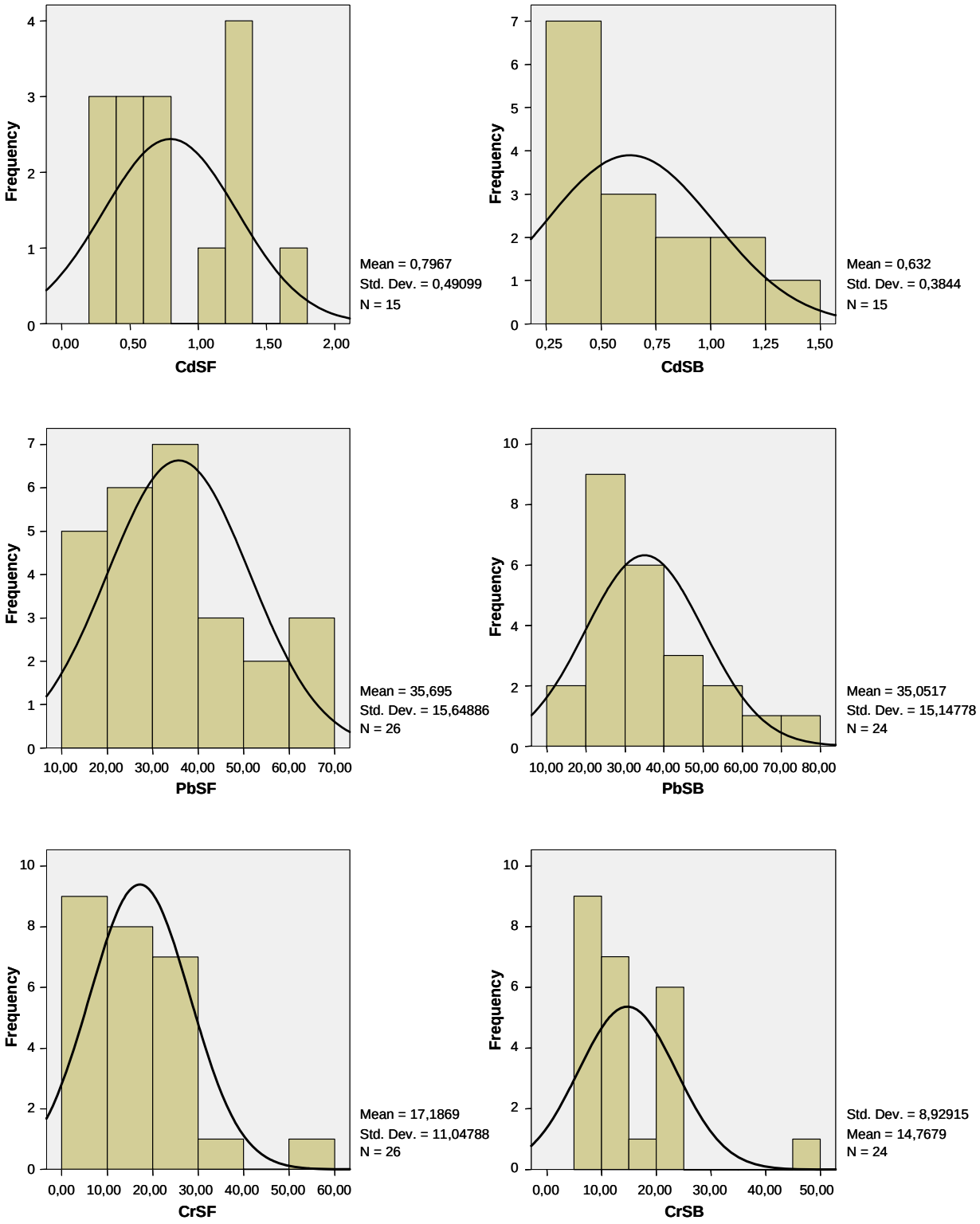


Figure 2 – Histograms of Cd, Pb and Cr for both SF and SB layer

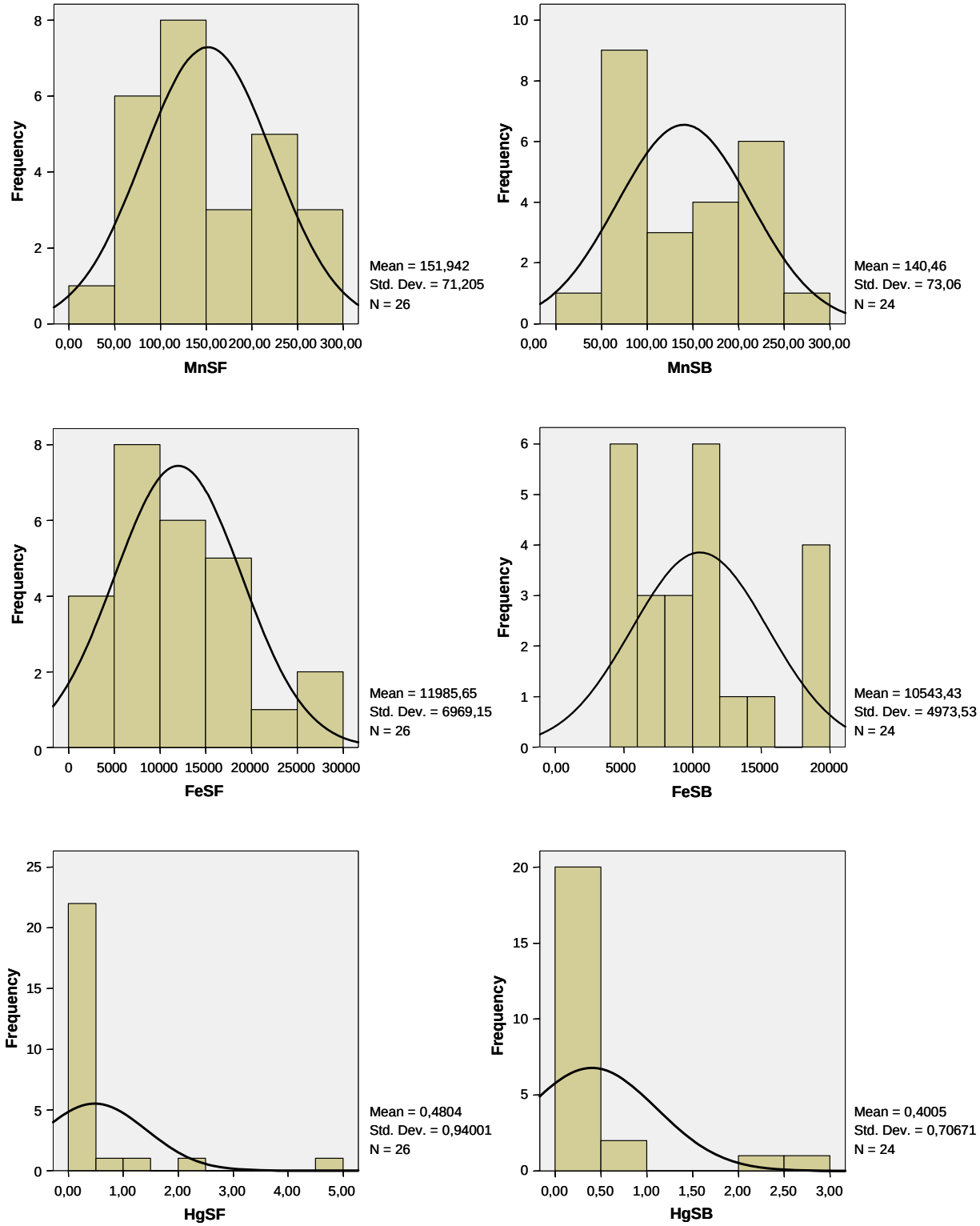


Figure 3 – Histograms of Mn, Fe and Hg for both SF and SB layer

Table 3- Pearson correlations (**. Correlation is significant at the 0.01 level (2-tailed); *. Correlation is significant at the 0.05 level (2-tailed))

		CuSF	NiSF	ZnSF	CdSF	MnSF	FeSF	PbSF	CrSF	HgSF
CuSF	Pearson Correlation	1	0.635**	0.641**	0.654**	0.683**	0.841**	0.531**	0.687**	0.164
	Sig. (2-tailed)		0.000	0.000	0.008	0.000	0.000	0.005	0.000	0.423
	N	26	26	26	15	26	26	26	26	26
NiSF	Pearson Correlation	0.635**	1	0.686**	0.595**	0.735**	0.764**	0.570**	0.795**	0.290
	Sig. (2-tailed)	0.000		0.000	0.019	0.000	0.000	0.002	0.000	0.150
	N	26	26	26	15	26	26	26	26	26
ZnSF	Pearson Correlation	0.641**	0.686**	1	0.251	0.529**	0.525**	0.691**	0.673**	0.471*
	Sig. (2-tailed)	0.000	0.000		0.366	0.005	0.006	0.000	0.000	0.015
	N	26	26	26	15	26	26	26	26	26
CdSF	Pearson Correlation	0.654**	0.595*	0.251	1	0.482	0.716**	0.185	0.633**	-0.137
	Sig. (2-tailed)	0.008	0.019	0.366		0.069	0.003	0.510	0.011	0.627
	N	15	15	15	15	15	15	15	15	26
MnSF	Pearson Correlation	0.683**	0.735**	0.529**	0.482	1	0.707**	0.608**	0.682**	0.137
	Sig. (2-tailed)	0.000	0.000	0.005	0.069		0.000	0.001	0.000	0.504
	N	26	26	26	15	26	26	26	26	26
FeSF	Pearson Correlation	0.841**	0.764**	0.525**	0.716*	0.707**	1	0.484*	0.842**	0.154
	Sig. (2-tailed)	0.000	0.000	0.006	0.003	0.000		0.012	0.000	0.453
	N	26	26	26	15	26	26	26	26	26
PbSF	Pearson Correlation	0.531**	0.570**	0.691**	0.185	0.608**	0.484*	1	0.621**	0.457*
	Sig. (2-tailed)	0.005	0.002	0.000	0.510	0.001	0.012		0.001	0.019
	N	26	26	26	15	26	26	26	26	26
CrSF	Pearson Correlation	0.687**	0.795**	0.673**	0.633*	0.682**	0.842**	0.621**	1	0.228
	Sig. (2-tailed)	0.000	0.000	0.000	0.011	0.000	0.000	0.001		0.262
	N	26	26	26	15	26	26	26	26	26
HgSF	Pearson Correlation	0.164	0.290	0.471*	-0.137	0.137	0.154	0.457*	0.228	1
	Sig. (2-tailed)	0.423	0.150	0.015	0.627	0.504	0.453	0.019	0.262	
	N	26	26	26	26	26	26	26	26	26

Annex V

Results obtained for organic contaminants in urban soils from Estarreja

Table 1 - Concentrations of PCB Congeners found in the Estarreja samples (µg kg^{-1})

Sample	PCB Congener																		
	1	5	18	31	52	44	66	101	87	110	151	153	141	138	187	183	180	170	206
1	0.27	0.15	0.00	0.24	0.01	bdl	0.09	0.07	bdl	bdl	0.16	0.30	0.21	0.33	0.09	bdl	0.34	0.09	0.02
2	0.15	0.16	0.20	0.49	0.34	0.17	0.13	1.04	0.10	bdl	0.15	0.07	0.26	0.16	0.71	bdl	0.11	bdl	0.36
3	0.15	0.09	0.14	0.10	0.30	bdl	bdl	0.53	bdl	0.29	1.01	3.30	1.64	2.08	0.83	0.78	1.41	1.44	1.32
4	0.16	0.11	0.12	0.22	0.20	bdl	bdl	0.08	bdl	0.09	0.30	0.46	1.62	0.26	1.26	0.86	0.18	1.44	1.46
5	0.20	0.27	0.32	0.44	0.59	bdl	bdl	bdl	bdl	bdl	0.34	0.25	0.62	0.23	bdl	bdl	bdl	bdl	0.62
6	0.49	0.22	0.29	0.27	0.45	0.09	0.27	0.17	bdl	0.11	0.36	0.54	0.32	0.36	0.36	0.45	0.21	0.31	1.32
7	0.25	1.57	0.26	0.44	0.30	bdl	0.23	0.93	bdl	bdl	0.66	0.33	0.24	0.35	bdl	bdl	0.66	bdl	2.78
8	0.23	1.24	0.30	0.49	0.31	0.16	0.29	0.10	bdl	0.18	0.29	0.69	0.22	0.51	0.33	0.05	0.25	0.21	0.21
9	0.23	0.39	0.16	0.33	0.32	0.10	0.06	0.10	bdl	0.28	0.21	0.66	0.84	0.52	0.14	0.08	0.75	0.21	0.48
10	0.41	0.23	0.16	0.37	0.36	bdl	bdl	0.17	bdl	0.29	0.27	0.54	0.74	0.72	0.16	bdl	0.37	0.23	0.89
11	0.08	0.26	0.11	0.18	0.29	0.15	bdl	bdl	bdl	bdl	0.15	bdl	bdl	bdl	bdl	0.22	bdl	bdl	bdl
12	1.65	1.09	0.48	1.48	0.66	0.12	0.17	0.36	bdl	0.08	0.26	0.69	3.63	0.54	0.19	0.02	0.51	0.31	0.60
13	0.37	0.21	0.33	0.50	0.28	0.07	0.27	0.04	0.04	0.03	0.09	0.15	0.67	0.17	0.44	0.34	0.14	0.23	0.35
14	1.17	0.39	1.49	1.00	0.81	0.20	0.24	0.37	0.83	1.04	0.60	2.20	0.67	1.58	0.40	0.14	1.04	0.35	1.69

bdl = below detection limit

Table 1 (cont.) - Concentrations of PCB Congeners found in the Estarreja samples (µg/kg)

Sample	PCB Congener																		
	1	**5**	**18**	**31**	**52**	**44**	**66**	**101**	**87**	**110**	**151**	**153**	**141**	**138**	**187**	**183**	**180**	**170**	**206**
15	0.73	0.35	0.45	0.28	0.92	0.33	0.53	0.60	0.15	0.59	0.89	2.52	1.96	1.57	0.36	0.20	0.75	1.19	1.12
16	0.49	0.33	0.24	0.73	0.52	0.23	0.29	0.27	0.06	0.27	0.84	1.54	5.27	0.99	0.25	0.09	0.48	0.27	4.18
17	0.10	1.07	0.52	1.05	0.48	0.14	0.26	0.25	bdl	0.12	0.34	1.02	0.73	0.64	0.53	0.62	0.38	0.19	0.84
18	0.35	0.96	0.73	1.60	0.76	0.67	0.20	3.31	0.74	2.54	5.43	12.6	5.01	8.15	1.76	0.96	5.15	2.47	1.79
19	1.79	0.42	0.58	0.52	0.77	0.21	0.52	0.31	bdl	0.16	0.44	1.33	1.17	0.85	0.21	bdl	0.45	0.36	0.42
20	0.35	0.38	0.35	0.59	0.71	0.14	0.56	0.84	0.21	0.48	1.24	3.04	1.44	1.73	0.43	0.22	0.95	0.69	0.88
21	0.17	0.20	0.33	0.02	0.12	0.08	0.15	0.40	0.13	0.28	0.63	2.16	1.03	0.90	0.24	0.16	0.56	0.32	0.50
22	0.11	0.16	0.07	0.63	0.21	0.07	0.10	0.15	bdl	0.09	0.28	0.80	0.28	0.56	0.37	bdl	0.20	0.15	0.44
23	0.19	0.14	0.94	2.06	0.28	0.18	0.11	0.75	bdl	0.12	0.15	0.48	2.44	0.31	0.38	bdl	0.63	0.90	1.03
24	0.43	0.53	0.26	0.41	0.28	0.20	bdl	0.23	bdl	0.14	0.28	0.94	0.83	0.54	0.22	bdl	0.27	0.22	0.41
25	0.33	0.77	0.44	0.34	0.48	0.18	0.33	0.29	0.38	0.30	0.43	1.36	2.60	0.96	0.44	0.33	1.62	1.72	1.18
26	0.88	0.17	0.21	0.46	0.48	0.15	0.11	0.25	0.11	0.38	0.58	1.39	1.16	0.95	0.23	0.09	0.46	0.25	0.15

bdl = below detection limit

Table 2 - Concentrations PAHs found in the Estarreja samples (µg kg^{-1})

Sample	PAHs															
	NP	**ACY**	**ACE**	**FLU**	**PHE**	**ANT**	**FLA**	**PYR**	**BAA**	**CRY**	**BBF**	**BKF**	**BAP**	**IND**	**DBAH**	**BGHI**
1	2.1	1.0	4.5	bdl	3.6	1.4	7.8	7.3	3.0	5.9	8.2	4.1	4.1	4.4	0.8	5.4
2	0.4	bdl	0.8	0.2	13.6	1.1	25.6	20.4	6.9	10.9	10.7	7.2	8.7	8.3	1.7	8.4
3	0.7	2.8	6.0	1.9	37.3	15.8	87.2	79.6	35.6	41.7	44.1	28.1	39.1	35.9	9.4	30.6
4	bdl	4.2	5.5	3.2	18	6.4	107	101	37.1	44.4	53.0	34.9	43.9	32.0	6.9	29.1
5	3.7	0.6	0.9	bdl	2.0	0.6	6.71	5.8	2.1	3.3	4.1	2.7	2.7	2.9	0.8	3.6
6	bdl	0.5	8.6	1.1	3.3	0.9	5.6	4.6	1.4	3.8	4.9	2.5	1.6	2.8	0.9	3.2
7	1.8	3.2	1.0	bdl	3.1	1.4	7.1	6.0	2.0	3.7	5.5	2.7	2.3	3.4	1.1	4.8
8	bdl	bdl	3.6	bdl	2.9	bdl	6.6	7.0	3.1	5.5	7.1	4.4	3.3	4.3	1.1	4.0
9	bdl	0.6	0.3	bdl	3.9	1.2	9.2	9.2	5.3	8.9	9.9	4.8	7.2	5.1	1.2	4.7
10	5.6	0.8	1.5	0.5	4.5	1.6	13.7	13.8	6.7	11.4	20.5	10.4	8.6	9.2	2.1	9.1
11	bdl	bdl	bdl	bdl	3.4	1.5	6.7	6.1	2.7	5.0	7.2	4.2	3.3	3.9	1.0	5.3
12	1.6	3.7	1.2	0.7	8.7	2.0	11.1	9.2	5.2	9.3	10.7	6.6	7.2	8.0	2.3	7.4
13	1.7	0.4	0.8	0.2	1.9	0.6	4.2	2.9	1.2	2.8	3.0	1.7	1.2	1.7	0.8	1.8
14	1.7	0.5	1.4	0.7	7.0	1.9	13.5	11.3	7.9	13.8	16.0	10.4	14.2	12.6	2.4	12.5

bdl = below detection limit

Table 2 (cont) - Concentrations PAHs found in the Estarreja samples (μg kg^{-1})

Sample	PAHs															
	NP	**ACY**	**ACE**	**FLU**	**PHE**	**ANT**	**FLA**	**PYR**	**BAA**	**CRY**	**BBF**	**BKF**	**BAP**	**IND**	**DBAH**	**BGHI**
15	bdl	0.5	bdl	0.4	5.8	0.7	11.4	9.8	4.3	8.3	8.3	4.3	4.0	4.5	1.0	3.9
16	0.5	2.3	1.1	0.4	5.7	2.3	16.5	15.0	5.6	9.5	13.4	6.6	6.2	6.9	2.1	6.2
17	0.9	3.4	0.9	1.7	19.2	4.1	47.4	40.3	22.9	28.6	35.6	29.4	33.1	21.6	5.9	17.0
18	0.5	0.7	1.8	8.8	17.7	14.8	5.9	4.9	4.9	8.2	11.7	6.5	4.8	4.4	1.2	4.0
19	6.4	18.1	1.5	5.9	188	15.3	282	200	27.1	81.8	88.0	54.1	54.2	39.4	12.1	48.2
20	1.9	35.9	3.6	7.6	139	34.5	472	406	114	175	147	144	142	93.3	24.4	77.3
21	0.4	0.6	1.1	0.6	2.9	0.9	6.8	4.4	1.5	3.5	3.6	2.2	1.7	1.7	0.5	1.8
22	1.0	0.6	0.8	1.3	2.5	1.1	5.7	4.5	1.7	3.6	5.9	3.6	2.0	2.9	0.7	3.1
23	1.2	2.3	0.6	0.3	5.4	4.3	18.9	17.5	5.5	9.5	12.0	8.9	9.7	7.2	1.6	6.5
24	0.5	0.9	0.3	0.3	2.5	1.2	7.6	7.3	3.8	5.9	5.8	4.3	4.7	3.6	1.0	2.7
25	1.9	4.9	0.2	0.2	1.9	0.6	6.1	7.0	12.3	20.7	17.8	13.2	7.6	10.8	2.6	9.7
26	1.5	1.1	5.1	0.4	7.1	2.0	24.9	25.0	9.5	13.5	17.6	93	12.2	9.1	2.1	8.7

bdl = below detection limit

Table 3 - Normality Test Kolmogorov-Smirnov, KS Distribution value, P value and the result for each sampling point

PCB congener	K-S Dist.	P	Normality Test
1	0.274	< 0.001	Failed
5	0.264	< 0.001	Failed
18	0.206	0.006	Failed
31	0.249	< 0.001	Failed
52	0.163	0.074	Passed
44	0.229	0.001	Failed
66	0.155	0.109	Passed
101	0.260	< 0.001	Failed
87	0.351	< 0.001	Failed
110	0.321	< 0.001	Failed
151	0.299	< 0.001	Failed
153	0.275	< 0.001	Failed
141	0.212	0.004	Failed
138	0.312	< 0.001	Failed
187	0.269	< 0.001	Failed
183	0.258	< 0.001	Failed
180	0.285	< 0.001	Failed
170	0.338	< 0.001	Failed
206	0.155	0.107	Passed

Table 4 - Normality Test Kolmogorov-Smirnov, KS Distribution value, P value and the result for each sampling point

PAHs	K-S Dist.	P	Normality Test
NP	0.233	< 0.001	Failed
ACY	0.357	< 0.001	Failed
ACE	0.285	< 0.001	Failed
FLU	0.322	< 0.001	Failed
PHE	0.389	< 0.001	Failed
ANT	0.346	< 0.001	Failed
FLA	0.388	< 0.001	Failed
PYR	0.374	< 0.001	Failed
BAA	0.327	< 0.001	Failed
CRY	0.345	< 0.001	Failed
BBF	0.326	< 0.001	Failed
BKF	0.344	< 0.001	Failed
BAP	0.339	< 0.001	Failed
IND	0.339	< 0.001	Failed
DBAH	0.367	< 0.001	Failed
BGHI	0.329	< 0.001	Failed